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A Survey of Present Methods Used to Determine the Optical Properties of Phosphors*,**

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A brief review of the theory of phosphors is given in terms of the electron-band picture of impurity semiconductors in order to show the reasons for researches designed to obtain the optical properties of phosphors. The automatic spectroradiometer is described since it is an instrument which yields so much information of value in phosphor research, development, and quality control. Some problems of spectroradiometer standardization are discussed in some detail, since the data obtained cannot be correctly interpreted by the I.C.I. system of color specification and interpretation unless satisfactory standards are maintained and used. A brief discussion is given of the application of the I.C.I. system to help in the choice of phosphors required to produce a suitable "white" for television cathode-ray tubes. Other researches discussed include the determination of phosphor excitation curves, the emission of light as a function of temperature and of time, and the correlation of spectral excitation and absorption data.

INTRODUCTION

THE determination of certain optical properties of phosphors is motivated by three broad objectives, which are (1) research, (2) development, and (3) quality control. In spite of the progress made during the past decade in the application of the electron energy band theory of solids to semiconductors and insulators, the systematic research needed to fill in the gaps in our knowledge of the experimental facts remains to be done. The development of new phosphors to fill specific practical needs, including such factors as efficiency, life under operating conditions, and specified spectral emission characteristics will be aided by the satisfactory theoretical interpretation of new experimental research, while at the same time reliance is given to the practical approach involving the systematic variation of impurities and processing techniques with results evaluated largely by empirical methods. Even here the theoretical explanations serve as a most useful guide to further empirical exploration. The need for the determination of certain optical properties of phosphors does not stop when a particular structure has been synthesized and a specific formula for production worked out. Constant vigilance is absolutely necessary as a means of quality control because many of the most useful phosphor properties can be materially interfered with by the accidental introduction of undesired impurities in concentrations as small as a very few parts in a million.

Some pieces of optical equipment, and in particular I refer to the spectroradiometer, are useful and in fact indispensable for research, development, and control in the major industries that produce such unbelievably large quantities of phosphors now used in cathode-ray tubes and fluorescent lamps. The monochromator is an important optical instrument used both in research and development of phosphors, in that a quantitative determination of excitation efficiency as a function of the wave-length of the radiation used to excite the phosphor is an important optical property.

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EDITOR'S COMMENT: This issue of the Journal is devoted entirely to papers on Fluorescence and Phosphorescence, most of which were presented at the meeting of the Optical Society of America held in New York on March 10–12, 1949. The papers have been collected and edited by DR. GORTON R. FONDA, who was in charge of the Symposium on Luminescence that was presented at the Optical Society Meeting.

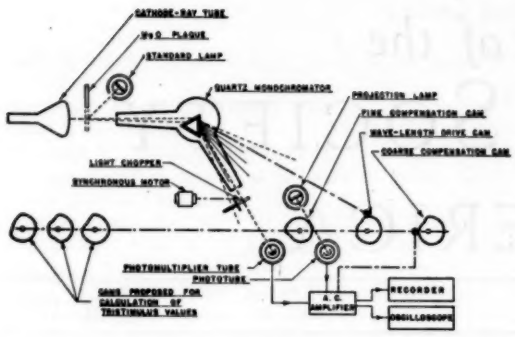

FIG. 1. Diagram—C.R.T. spectroradiometer. (Sylvania Electric Products, Inc., Physics Laboratories.)

The electron multiplier type of photo-tube, now almost universally used as a means of quantitatively determining the radiant output of phosphors, has proven to be an indispensable accessory for a very large proportion of all measurements made in the past seven or eight years.

Optical observations made in the study of atomic and molecular excitation and radiant energy emission involve the time history and the temperature conditions very indirectly as compared to the general case for phosphors. In the latter case, the time history of excitation, the time of observation, and the temperature history during both excitation and observation are of utmost importance and, in fact, serve as controllable variables through which the basic facts concerning the electronic band structure of the solid are exhibited.

A BRIEF REVIEW OF THE THEORY OF PHOSPHORS

Nearly all practical phosphors are crystalline in structure and are very dependent on the presence and suitable disposition of selected impurities known generally as "activators." In certain types of phosphors, of which the silicates are typical, the activator fits into the lattice in a substitutional position for one of the atoms normally found in the basic crystal structure. Phosphors of which zinc sulfide is typical, require concentrations of activator that constitute a very small fraction of 1 percent, since the necessary impurities take positions interstitially between the atoms of the crystalline substance. The outermost or valence electrons of a perfect crystal move from atom to atom throughout the crystal even at extremely low temperature. In spite of this freedom of motion, the application of small differences in potential to the crystal does not result in conductivity, because the electrons are so crowded into their only available quantum states that at low temperatures and with moderate electric fields the electrons cannot cross the energy gap, in which there are no available electronic energy levels, to find the greater freedom of motion associated with the higher "conduction" levels of the system. Support for this view of the electronic structure of insulators may be derived from experiments on the optical absorption of these crystals. If the energy ($h\nu$) of the light quantum is insufficient to cause an electronic transition from an occupied to an unoccupied state, then the optical absorption of the crystal is small. Thus, the measurement of the optical absorption of single crystals, or even of polycrystalline material when samples of uniform particle size and variable thickness may be used, serve to give direct information concerning the energy level system of the phosphor.

The introduction of impurities into the crystal generally modifies in a measurable way the absorption characteristic of the material. This fact indicates the importance of the close coordination needed to relate the chemistry and production of phosphors to the optical absorption characteristics of the substance.

By far the most common means of phosphor excitation depend either on the absorption of energy by the electrons from electromagnetic radiations in the visible or in the ultraviolet range of the spectrum, or else by the absorption of energy that results from electron bombardment. Although many secondary effects are associated with phosphor excitation, the primary process involves the transfer of electrons from the stable valence electron band or from bound electrons located at impurity centers into normally unoccupied electronic levels of the conduction band. As a result of this transfer of the electron into a conduction band, a negative charge carrier becomes mobilized, and, in addition, the absence of an electron in the normally filled valence band is the equivalent of mobilizing a positive charge carrier or an "electron hole." The reverse process is the recombination of an electron with an electron hole and the simultaneous conversion of the potential energy thus temporarily stored into the radiant energy of a light quantum or into the vibrational energy of the atoms nearby.

In many respects, the situation may be compared to the ionization of a gas in the plasma of a gas discharge. In that case, both the positive ions and the electrons are mobile and can maintain nearly equal volume concentrations, and yet free space recombination is a relatively uncommon occurrence. If the ion becomes attached to an insulating wall, or if the electron becomes attached to an otherwise neutral atom or molecule, then recombination takes place very readily. A similar situation occurs in phosphors, and other insulators and semiconductors. If the electron hole becomes trapped at an impurity atom, while the electron itself remains free, recombination is likely to occur. In a similar manner, electron holes that migrate to the surface of the crystal attract electrons and recombine with them there. Electrons may become trapped in other types of impurity centers, but, nevertheless, recombination can take place because of the mobility of the holes. The last of the simple cases involves the trapping of both the holes and

the electrons. A "meta-stable" situation is thus created in which recombination is inhibited and becomes extremely temperature sensitive, since it is by means of the absorption of temperature energy by the trapped electrons or holes that they are restored to mobility.

An investigation of spectral emission data, interpreted in a manner thus briefly described, permits the observer to evaluate quantitatively the energy jump that the electron takes upon recombination. Since the energy jumps for a given transition in a particular phosphor are not exactly the same throughout the volume of the crystal, the radiant energy emitted is not confined to a narrow band of wave-lengths, but spreads on each side of a most probable energy transition to create a relatively broad continuous set of emitted wave-lengths. Thus, the determination of the spectral emission characteristic of a phosphor stands very high in the interests of all investigations, including research, development, and quality control.

The lines of investigation that yield detailed information in support of the theoretical picture thus described, include the determination of excitation efficiency as a function of the wave-length of the exciting radiation and as a function of the electron energy and current density used for excitation. A quantitative determination of the influence of temperature on the light output and of the time changes of light output can be interpreted to give quantitative data on the number and energy distribution of the trapping states. Simultaneous determination of the electrical conductivity of crystals during excitation yields valuable detailed material for analysis.

SPECTRORADIOMETERS

Basically, a spectroradiometer is a low resolution spectrometer designed to give quantitative information concerning the radiant power at the exit slit found in a relatively wide band of wave-lengths. Thus, accuracy in wave-length specification is seldom as good as 1 percent and is often allowed to spread as much as ± 5 percent from the nominal wave-length value. This sacrifice in wave-length resolution is necessary in order to have sufficient power delivered to the detector to make quantitative measurements relatively easy. The fact that most practical spectroradiometers have such poor wave-length resolution becomes an objection only under the relatively rare circumstance that the spectral emission characteristic of the phosphor is one that has important structural details which would be completely lost to the observer who places his entire reliance upon a low resolution instrument.

The invention of the multiplier photo-tube as an electronic detecting element made it possible to increase the speed with which spectroradiometric measurements can be made and, in fact, permitted the development of automatic recording instruments that give valuable quantitative information ready for use and analysis in a matter of minutes. The first such instrument was that developed by Dr. Zworykin[1] and his group at RCA.

The Zworykin instrument has been further developed by Leverenz and Shrader and has served to yield a vast quantity of recorded spectroradiometric data. Although this instrument was designed to have approximate corrections included automatically to yield a record of the radiant power output from an excited phosphor per unit range in wave-length as a function of the wave-length, it has not been found necessary for them to have high accuracy in this respect. The instrument has been used primarily as a means of discovering *changes* in the spectral output that follow systematic changes in composition or in processing. These changes may be exhibited with all the accuracy required for practical purposes, without the development of a system which makes perfect compensation for such factors as slit-width variation, light absorption in the optical parts of the instrument, and variations in photo-multiplier response.

Instruments of this type may be made very versatile, so that an analysis can be given for phosphors excited either in a demountable cathode-ray tube arrangement in which some 6 or 8 samples may be prepared for study at a given time, or the light may be derived from a phosphor used in a completed cathode-ray tube or from phosphors excited by the absorption of ultraviolet radiation. Instruments used in connection with the development of phosphors for fluorescent lighting may also be adapted to receive and analyze the light produced in this manner.

A unique instrument has been developed for use under the direction of Dr. L. Headrick of the RCA Victor Division,[2] Lancaster, Pennsylvania. A twelve-inch cathode-ray tube, manufactured with a long persistence P-7 cascade phosphor type of screen, is used to record the radiant output as a function of the wave-length. The approximate time for the production of a complete record is 13 sec. and the pattern remains visible for at least 1 or 2 min. Since it is possible to shift the samples being investigated very rapidly, advantage is taken of

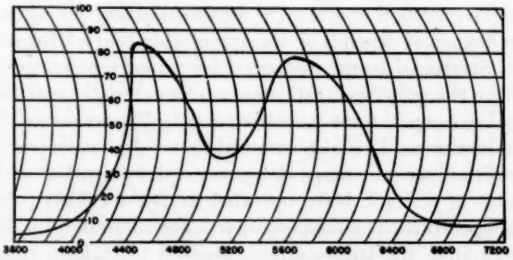

FIG. 2. Superposition of test runs 1, 2, and 3 P-4 phosphor in 10BP4 tube taken on spectroradiometer of Sylvania Electric Products, Inc.

[1] V. K. Zworykin, J. Opt. Soc. Am. **29**, 84 (1939).
[2] A. E. Hardy, Trans. Am. Electrochem. Soc. **91**, 221 (1947).

the fact that two or three records can be run on in rapid sequence and thus permit a direct comparison between samples. It is evident that a recorder of this type is very suitable for quality control, in that one of the samples may be the "standard" and the other sample a phosphor or phosphor blend which must come within certain, rather narrowly specified, limits of the standard pattern in order to be acceptable. Whenever a permanent record of the observations is desired, a camera mounted directly on the instrument is used to photograph the pattern.

Considerable care has been taken in the construction of this instrument and in its calibration, in order to warrant its use as a means of color identification by the I.C.I. color system. The need for instrumental accuracy, when the data are to be used for color specification, has also been recognized by Bowie and Martin.[3] Figure 1 shows by diagram the main features of the Sylvania automatic spectroradiometer. A typical record of the blended phosphor identified as P-4 and described as being television white is shown in Fig. 2. This figure also serves to indicate the reproducibility of the recording instrument in that the line has been widened slightly, so that three separate runs on the same material are covered completely by the line shown.

Attention should be directed to a recent development of Dr. F. J. Studer,[4] as a result of which an automatic spectroradiometer has been designed for service in the Research Laboratory of the General Electric Company. This equipment has the advantage of noteworthy simplicity and at the same time comparison tests showed excellent agreement between the automatically recorded spectral power distribution and the point by point study made by Dr. B. T. Barnes in which a double monochromator was used. Since the wave-length band transmitted through the Studer instrument may be of the order of 5 to 10 millimicrons, some care must be taken with such low resolution equipment when it is used with phosphors that change intensity rapidly with wavelength.

STANDARDIZATION OF SPECTRORADIOMETERS

The method used for the standardization of spectroradiometers depends on the assumption that all Bureau of Standards lamps calibrated for "color temperature" have the same spectral emission characteristic over the entire range in wave-length from 380 millimicrons to 720 millimicrons. It is also assumed that the relative power emitted per unit range in wave-length is identical with that of a black body operated at the specified color temperature. The lamp standards are calibrated by determining the lamp current required to make a color match with a B. of S. standard lamp. It is well known that two sources of radiant energy can have distinctly different relative spectral power distributions and yet have exactly the same color as interpreted by a human observer. The standard lamps generally used are coiled filament projection lamps and are therefore neither true black body sources nor tungsten emission sources. It follows, therefore, that if two lamps that differ in mechanical structure in terms of the spacing between coils and the effect of cooling at the filament supports have the same color, they will nevertheless differ appreciably in their true relative spectral power emission properties. It is impractical to consider the use of a high temperature black body source for standardization. It might even be considered impractical to use a large area ribbon filament as a working standard in a particular laboratory. A practical solution for the standardization of the spectroradiometers could, however, be worked out along the following lines. First, the spectral emissivity of tungsten viewed in a direction normal to the surface must be known for the entire range of wave-length and temperature of importance. The data published by Forsythe and Worthing[5] are in excellent agreement with recently determined, but still unpublished, data obtained by the writer.[6] The Forsythe and Worthing data are well represented by the empirical formula:

$$e_{\lambda T}=0.5364+5.24\times10^{-6}T-(9187+3.822T)\times10^{-8}\times\lambda.$$

In this equation, $e_{\lambda T}$ is the spectral emittance and is a function of the wave-length expressed in millimicrons and the temperature expressed in degrees Kelvin. The true temperature of a tungsten ribbon can be determined from an accurate measurement of the "brightness" temperature evaluated by a well-calibrated optical pyrometer. The wave-length at which the brightness match is made must be known, and the emittance can be obtained from the above equation as a result of successive approximations. An optical system can be arranged so that the only light that enters the spectroradiometer comes from the uniformally hot part of the ribbon filament. If consideration is given to the absorption of the glass envelope surrounding the ribbon filament, and if geometrical factors are also taken into account, then the absolute spectral irradiance can be computed. In general, it is only the *relative* spectral irradiance that is needed and the method by which this information is used involves the introduction of gain-correcting adjustment, as indicated in the schematic of Fig. 1, so that the recorded output curve coincides with the calculated relative irradiance curve.

The second step in standardization would involve the substitution of a particular standard "color-temperature" lamp of the coiled filament type and the running of a spectral emission curve for this lamp. After having once made a determination of the true relative spectral emission of this practical secondary standard, one can

[3] R. N. Bowie and Alfred E. Martin, Proc. I.R.E. **36**, 1023 (1948).

[4] Frank J. Studer, J. Opt. Soc. Am. **38**, 467 (1948).

[5] W. E. Forsythe and A. G. Worthing, Astrophys. J. **61**, 146 (1925).

[6] W. B. Nottingham and W. E. Mutter, Phys. Rev. **47**, 1261 (1948); $e_{\lambda T}=0.5308+5.24\times10^{-6}T-(9187+3.90T)\times10^{-8}\times\lambda$.

then use it to maintain the instrument in calibration without recourse to the primary ribbon filament standard.

I.C.I. INTERPRETATION OF THE SPECTRORADIOMETRIC DATA

Through the cooperative activity of the International Commission on Illumination (I.C.I.), a system of color specification has been developed by which the determination of two numbers is sufficient to identify a color appearance to the so-called "standard" observer. These two numbers are known as the "trichromatic coefficients." In the application of this system, use is made of three sets of numerical data represented by the symbols $\bar{x}_\lambda$, $\bar{y}_\lambda$, and $\bar{z}_\lambda$. The numerical values of these functions are available,[7] and the arithmetical calculation in which they are used is represented by the three equations:

$$U=\int_0^\infty \bar{x}_\lambda h_\lambda d\lambda,$$

$$V=\int_0^\infty \bar{y}_\lambda h_\lambda d\lambda,$$

$$W=\int_0^\infty \bar{z}_\lambda h_\lambda d\lambda.$$

In these equations h_λ represents the relative spectral power distribution of the source being evaluated. The trichromatic coefficients are defined finally by the expressions:

$$x=U/(U+V+W), \quad y=V/(U+V+W).$$

The numerical evaluation of the three quantities U, V, and W may be carried out in either one of two ways as soon as the spectral power distribution similar to that shown in Fig. 2 has been determined. The one method involves the direct graphical integration of the product curve obtained by the direct multiplication of the particular tristimulus distribution function $\bar{x}_\lambda$, $\bar{y}_\lambda$, or $\bar{z}_\lambda$ by the h_λ function. The second method of computation involves the "selected ordinate" summation. For each of the tristimulus distribution functions, tables of wavelength values at which the ordinate of the spectral power distribution curve should be evaluated have been prepared.[8] Bowie and Martin have prepared transparent sheets of plastic on which the 30 selected abscissa lines are drawn for each of the tristimulus distribution functions. They superimpose these engraved lines over the record similar to Fig. 2 and tabulate the ordinate values at each intersection between the engraving and the relative power distribution curve of the phosphor under examination. The simple sum of the 30 numbers thus obtained is directly proportional to the value of U, V, or W depending on which engraving is used. In general, the use of the selected ordinate method is superior in terms of convenience and accuracy to the straight integration scheme.

The use to which the trichromatic coefficients x, y may be put is well illustrated by Figs. 3 and 4, in which data published by Hardy[9] are shown by way of illustration. The reader may be reminded that in the diagram of Fig. 3, the solid line marked "pure spectrum locus" closed at the lower end by a straight line joining the extreme blue region with the extreme red region, encloses the entire domain of realizable colors. The pure spectrum colors lie on the locus line and any combination whatsoever of spectrum colors used to make up a particular spectral power distribution must lie inside of the domain of realizable colors, because a mixture of any two of them results in a representative point in the diagram that lies on the straight line joining the components of the mixture. This rule of color mixture also applies, as is illustrated in Fig. 4, to the mixing of broad band sources such as we have for excited phosphors just as well as for the narrow band sources associated with individual spectrum colors.

Although qualitative inspection of the light emitted by phosphors of systematically variable composition may be recognized easily, the quantitative representation shown in Fig. 3 for the various solid solution proportions of ZnCdS:Ag for the range in CdS propor-

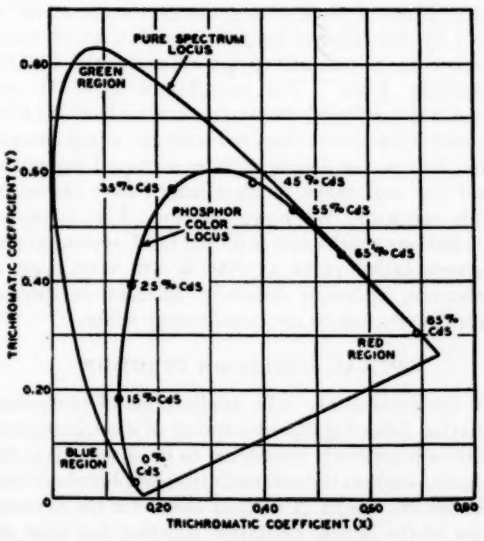

FIG. 3. I.C.I. color system. Mixture diagram showing ZnCdS:Ag phosphor color locus as a function of percent CdS. (A. E. Hardy, RCA Review.)

[7] D. B. Judd, J. Opt. Soc. Am. **23**, 359 (1933). A. C. Hardy, *Handbook of Colorimetry* (The Technology Press, M.I.T., Cambridge, 1936). For discussion of system, W. B. Nottingham, Radiation Lab. Rep. 804 (December, 1945) NDRC, Div. 14, OEMsr-262 "Notes on photometry, colorimetry and in explanation of the centibel scale."

[8] Committee on Colorimetry, J. Opt. Soc. Am. **34**, 633 (1944).

[9] Austin E. Hardy, RCA Review **8**, 554 (1947).

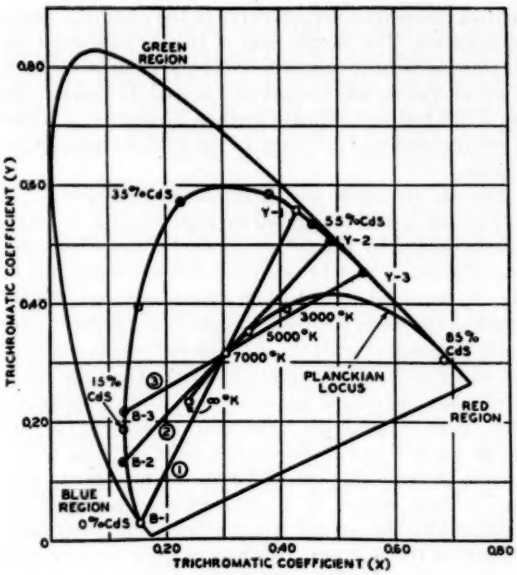

FIG. 4. Mixture diagram showing three phosphor pairs. (A. E. Hardy, RCA Review.)

tion from 85 percent down to 0 percent is of great practical value.

Although none of the phosphors found on the "phosphor color locus" line would be acceptable for a television cathode-ray tube as being "white," an infinite number of combinations could be chosen that would be indistinguishable in their whiteness by the "standard" observer. Three of these combinations are illustrated in Fig. 4 by the straight lines 1, 2, and 3, all of which intersect at a common point close to the 7000°K "Planckian locus." The coordinates $x=0.333$ and $y=0.333$ locate the representative point which would be obtained if the source observed were an "equal-energy" white, that is, the source radiates an equal amount of power per unit range in wave-length over the entire visible spectrum. We note, therefore, that phosphor combinations which analyze by the I.C.I. system to give a representative point at 7000°K are very close in appearance, although definitely different in spectral power distribution to the equal-energy white.

OPTICAL EXCITATION FUNCTION

In the cathode-ray tube applications of phosphors, excitation following the absorption of electromagnetic radiation is generally considered to be of secondary importance, whereas the reverse is true for phosphors used in fluorescent lamps. A method useful for the determination of the optical excitation function has been described by Fonda and Studer,[10] in which the light from the continuous spectral distribution of power from a hydrogen arc is passed through a monochromator and allowed to fall directly on the thin deposit of phosphor under investigation. A sufficient fraction of the light emitted by the phosphor passes through it and also through the glass plate upon which the phosphor is deposited to give rise to sufficient photoelectric current in the detecting multiplier photo-tube to serve as an accurate measure of the luminescence of the phosphor. This information, combined with the knowledge of the relative power impinging on the phosphor as a function of wave-length, allows for the quantitative determination of the relative efficiency of the different wave-lengths in the spectrum for the excitation of luminescence. Results so obtained are significant both from the theoretical and the practical points of view. Systematic changes in the excitation curve depending on the nature and the quantity of activating agent have been observed.

Fonda and Studer also have shown the value of a determination of the spectral absorption characteristic of a phosphor by studying its diffuse reflectance. They have found useful correlations between the absorption spectrum, the excitation spectrum, and the phosphor composition and treatment. These and similar data are needed on a wide variety of phosphors in order to fill in quantitative information needed for the formulation of an adequate theory to account for the optical properties of phosphors.

PHOSPHORESCENCE AND OTHER STUDIES INVOLVING TIME AND TEMPERATURE

One of the most interesting developments of the past decade has been the study of phosphor "glow curves." The experiment involves the excitation of a phosphor by ultraviolet light while it is maintained at a very low temperature. In general, luminescence will be observed during the excitation period but immediately thereafter the phosphorescence will fall rapidly to a negligible value. However, if the phosphor is permitted to warm up gradually, measurable phosphorescence will very likely develop in the temperature range 100° to 200°K and a reproducible curve will be obtained for the power radiated as a function of the temperature. Obviously, such curves depend on the constant time rate of change of temperature used in the experiment and on the composition and structure of the phosphor. A summary of some of the work and a discussion of the theory may be found in the report by Garlick[11] and the paper by Williams and Eyring.[12]

Equipment designed with all of the refinements necessary to get good quantitative data at very slow rates of increase in temperature with time, could also be used to determine the time change in phosphorescence at fixed

[10] Gorton R. Fonda and Frank J. Studer, J. Opt. Soc. Am. **38**, 1007 (1948).

[11] G. F. J. Garlick, Chapter 5, p. 87 of *Solid Luminescent Materials* by G. R. Fonda and F. Seitz (John Wiley and Sons, Inc., New York, 1948).

[12] Ferd Williams and Henry Eyring, J. Chem. Phys. **15**, 289 (1947).

points in temperature. Outside of the studies made at room temperature, relatively little has been done on the decay of phosphorescence at low temperature. Another closely related line of experimentation would involve the maintenance of the excited phosphor at a very low temperature and the observation of the nature of the phosphorescence decay under the stimulation of monochromatic infra-red radiation. It is evident that all of these studies, if applied to a given sample of phosphor, would yield most valuable information from which the number and energy depth of the electronic trapping states could be determined.

Extensive studies were made during the past few years on the natural and stimulated decay properties of phosphorescent substances, with the major attention given to the development of phosphors useful for particular military applications. These studies demonstrated that broadly speaking, there are two types of decay most commonly found, which are: (1) "exponential" and (2) "inverse time." These decay types are easily identified by the fact that the exponential yields a fairly good straight line when the logarithm of the phosphorescent output is plotted against a linear time scale. The slope of the line thus obtained is very nearly independent of the degree of excitation and the length of time of excitation over quite wide ranges of these variables. As a class, the silicates, the fluorides, and the tungstates generally exhibit exponential decay curves. The sulfides fall in the "inverse time" grouping and here an approximately linear plot is obtained if the logarithm of the phosphorescent power is plotted as a function of the logarithm of the time of observation. The slopes of the observed lines vary from approximately 0.8 to 2.0. Since the characteristic slope for a simple bimolecular process would have been 2, it is evident that phosphorescence cannot be explained in such a simple manner. Considerable experimental data have been made available[13] recently and it is probable that additional information will be accumulated slowly, since there are in existence in the various research laboratories equipment for making such studies. Relatively little attention is being given to this matter at present.

CONCLUDING REMARKS

The means for the determination of many of the optical properties of phosphors have been developed and enough information obtained to show that researches in this field have in reality just begun. In spite of the complications, various approaches yield interlocking parts to this scientific jigsaw puzzle. More attention is being given at present to the quantitative determination of the spectral power distribution emitted by phosphors and determined by means of automatic spectroradiometers. It is understandable that so much emphasis is placed on this particular line of research, because it is so important from all of the motivating points of view that include research, development, and product control.

[13] G. R. Fonda and F. Seitz, *Solid Luminescent Materials* (John Wiley and Sons, Inc., New York, 1948). Also Soller, Starr, and Valley, Cathode Ray Tube Displays (McGraw-Hill Book Company, Inc., New York, 1948), Radiation Lab. Series, Vol. 22. (See Chapter 18, "Screens for cathode ray tubes" by W. B. Nottingham.) Kröger, Hoogenstraaten, Bottema, and Botden, Physica **14**, 81 (1948) and F. A. Kröger and W. Hoogenstraaten, Physica **14**, 425 (1948).

Review of the Interpretations of Luminescence Phenomena*

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After a brief discussion of the importance of the interpretations of luminescence phenomena to the design and improvement of phosphors and to the modern electronic theory of solids, the general theoretical approaches and models are presented. The particular scopes of application and limitations of the electronic band theory model and the configurational coordinate model are stressed. Phenomenological analyses of temperature-quenching of efficiency and afterglow, two-stage afterglow, thermoluminescence, electron retrapping, and positive hole migration, that have been developed and emphasized during the past decade, are reviewed and compared with experimental data. In addition, the atomistic interpretations that have been qualitatively developed and are being quantitatively refined are briefly presented. The need for an absolute theory of luminescence, by means of which the significant properties of phosphors can be quantitatively computed from first principles, is emphasized.

I. INTRODUCTION

THE interpretations of luminescence phenomena are important for two reasons: (1) Insofar as the precise mechanism of luminescence is known, it is possible to design and improve phosphors from fundamental considerations; (2) The detailed understanding of luminescence provides insight into electronic processes in solids in general.

The present status of the theory of luminescence in phosphors is quite good. The electronic theory of solids has provided a qualitative explanation of many luminescence phenomena, and during the past decade a quantitative phenomenological theory to explain and correlate specific properties has been developed. However, an absolute theory of luminescence that will provide the techniques for calculating the magnitudes of the significant luminescent properties from fundamental principles has barely been initiated.

II. THEORETICAL APPROACHES AND MODEL

The phenomenological approach is applied as follows: suggested by quantitative experimental results and guided by the theory of solids, a model is proposed; dynamical equations are formulated; analytic expressions for the observables in terms of the variables of the model are derived and applied to the experimental data using adjustable parameters; and finally the magnitudes of the parameters are interpreted. The absolute or atomistic approach is applied by utilizing the results of the phenomenological approach to simplify the problem and then by calculating from first principles and the known interactions of electrons and ions the magnitudes of significant luminescent properties, using data on the properties of free ions and pure solids whenever possible.

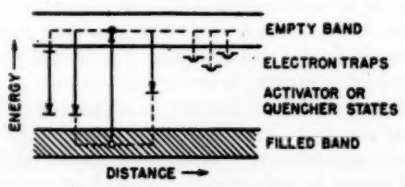

FIG. 1. Composite band theory model for luminescence.

Practically all interpretations of luminescence phenomena have been based either implicitly or explicitly on some modification of the band theory model or of the configuration coordinate model.

The band theory model is based on the general quantum mechanical treatment of the interaction of valence electrons with the three-dimensional periodic potential of the crystal lattice. In this system, neglecting the exchange forces between the electrons, the energy levels consist of broad bands of allowed energies separated by broad bands of forbidden energies.[1-2] In their states of lowest energy, the electrons which do not form a complete valence group should be tightly bound and exactly fill up one of the bands of allowed energies in order that a substance be an electronic semiconductor, the class of solids to which phosphors belong. More precise energy diagrams contain narrow continuous bands lying in the forbidden region between the Bloch-Wilson bands. In these states, which are computed by the Heitler-London approximation, the excited electron and the positive hole it leaves in the lowest band—together called an "exciton"—are closely coupled and move together, transporting no charge.[3-4] However, just as the electrical properties of real electronic semiconductors are dominated by impurities and crystal defects,[5] the luminescent properties of phosphors are dominated by discrete localized activator and quencher levels and trapping states.

Figure 1 is a composite band theory model for luminescence.[6-13] Optical absorption may occur by excitation

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[3] J. Frenkel, Phys. Rev. **37**, 17, 1276 (1931).
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[5] A. H. Wilson, Proc. Roy. Soc. **134**, 277 (1932).
[6] R. P. Johnson, J. Opt. Soc. Am. **29**, 283, 387 (1939).
[7] N. Riehl, *Physics and Applications of Luminescence* (Verlag. Julius Springer, Berlin, Germany, 1941), p. 108.

of an electron from the filled band or from an impurity level to the empty band. Both the excited electron and the positive hole may migrate through the lattice until recombination and emission occurs when the positive hole is captured by the activator level and the electron is in the vicinity of the activator ion. Between absorption and emission electron trapping may occur. If the absorption and emission processes involve transitions between states peculiar to the activator ion and the energy bands of the lattice are not involved, the band theory model is not particularly applicable. In other words, the band theory model is especially suitable for interpreting luminescence phenomena involving the transport of electrons through the lattice, for example: positive hole migration, electron trapping remote from the activator ion, and photo-conductivity. A bimolecular mechanism of phosphorescence is suggested by the band theory model because the rate of recombination depends on both the concentration of excited electrons and on the concentration of positive holes. The principal limitation of the model is that the energy bands and levels are characteristic of a particular atomic configuration so that the atomic rearrangements that occur during luminescence are ignored. Therefore, the model does not indicate the origin of the large quantum energy difference for absorption and emission and does not suggest the pronounced temperature-broadening of excitation and emission energies.

The configuration coordinate model emphasizes atomic rearrangements. Diagrams of energy *versus* a position coordinate have been used in problems of molecular spectra and the rates of chemical reactions. In these applications, the configuration coordinate can usually be precisely specified as an interatomic distance. To describe completely the atomic rearrangements involved in electronic processes in solids would require energy contours in configuration space having three times as many coordinates as there are particles involved. In describing the transitions and rearrangements occurring in luminescence phenomena, a useful simplification is to define a "center" as the ion undergoing the electronic transition plus the group of neighboring ions participating in the rearrangements, and then specifying to a first approximation the coordinates of the centers by a single configuration coordinate. Figure 2 is a comprehensive configuration coordinate model for luminescence.[14–18] The three types of states—

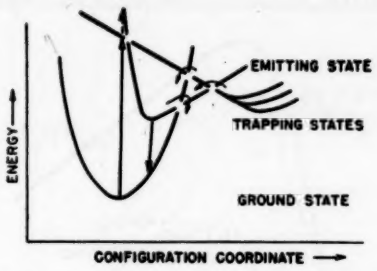

FIG. 2. Comprehensive configuration coordinate model for luminescence.

the ground, the trapping, and the emitting states—represented by the contours, may have different multiplicities. Electrons in one state tend to remain in that state where the contours apparently cross and optical transitions between the states are to some extent forbidden. In the simple luminescence involving only the ground and emitting states, absorption consists of an electronic transition directly to the emitting state. This occurs maintaining the atomic configuration of the ground state because the excitation process, according to the Franck-Condon principle, takes place quickly before the ions have a chance to move. Following excitation, the redistribution of electronic charge causes the atoms to shift to new equilibrium positions minimizing the total energy. The excess energy is propagated from the center as elastic waves. Emission then occurs maintaining the atomic configuration of the emitting state and another rearrangement follows. Competing with the emission process is an activated radiationless process for returning to the ground state. In more complex luminescence involving trapping states, excitation does not occur directly to the emitting state but instead an activated rearrangement is prerequisite to emission. The configuration coordinate model clearly emphasizes the rearrangement energy as the origin of the difference in excitation and emission energies. In addition, the model indicates that the atomic configurations other

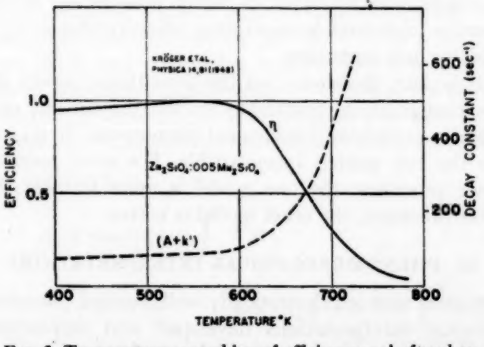

FIG. 3. Temperature quenching of efficiency and afterglow.

[8] M. Schon, Zeits. f. Physik **119**, 463 (1942).
[9] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. **A184**, 367 (1945).
[10] R. C. Herman and C. F. Meyer, J. App. Phys. **17**, 744 (1946).
[11] F. A. Kröger, Physica **14**, 427 (1948).
[12] Klasen, Ramsden, and Quantie, J. Opt. Soc. Am. **38**, 60 (1948).
[13] G. F. J. Garlick and A. F. Gibson, Proc. Phys. Soc. **60**, 575 (1948).
[14] A. von Hipple, Zeits. f. Physik **101**, 680 (1936).
[15] R. W. Gurvey and N. F. Mott, Trans. Faraday Soc. **35**, 71 (1939).
[16] F. Seitz, Trans. Faraday Soc. **35**, 79 (1939).
[17] P. Pringsheim, Rev. Mod. Phys. **14**, 132 (1942).
[18] F. E. Williams and H. Eyring, Phys. Rev. **69**, 257 (1946) and J. Chem. Phys. **15**, 289 (1947).

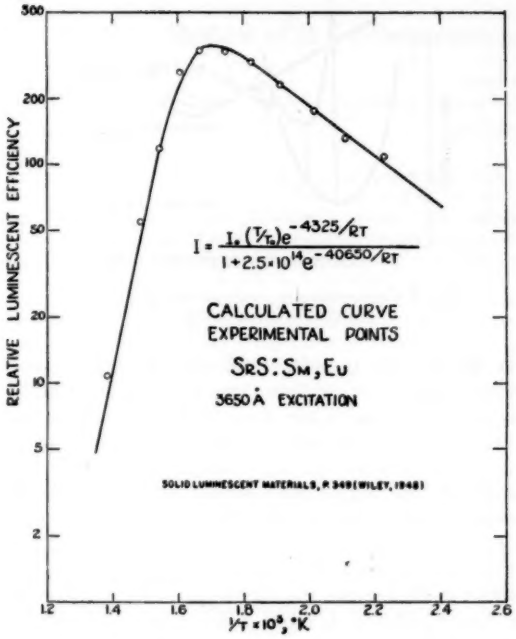

FIG. 4. Effect of competing radiationless processes and electron trapping on temperature-dependence of luminescent efficiency.

than the one of lowest energy have finite probabilities so that all optical transition energies will be broadened and the broadening will be strongly temperature dependent. Finally the model draws attention to activated rearrangements and competing radiationless processes. Because the configuration coordinate model treats each center as independent, the rates of excitation, rearrangement and emission, as well as the competing radiationless processes, would seem to depend only on the number of centers in the state undergoing the change, and therefore, a monomolecular mechanism dominating luminescence phenomena is strongly suggested. The model has a limited application because it obscures the mechanisms of transport of charge through the lattice, thereby inadequately explaining photo-conductivity or positive hole migration.

It is clear, therefore, that the band theory model and the configuration coordinate model complement each other in explaining luminescent phenomena. In no way are the two models incompatible. For some luminescence processes, the one model is more suitable; for other processes, the other model is better.

III. PHENOMENOLOGICAL INTERPRETATIONS

Several selected theoretically well-founded phenomenological interpretations developed and emphasized during the past decade to explain specific luminescence phenomena will now be reviewed. The model most appropriate to each phenomenon will be used in the analyses. The theoretical results will be tested against experimental data.

A. Temperature-quenching of efficiency and afterglow: Kröger and co-workers[19, 4] have recognized that the competition between radiative and non-radiative de-excitation of an excited center must affect both the temperature-dependence of afterglow and of luminescent efficiency. From Fig. 2 considering a simple phosphor having negligible electron traps, it is apparent that the rate of decrease in concentration of centers in the emitting state on removing the excitation is:

$$-(dn/dt) = An + k'n = (A+k')n.$$
$$\therefore\ n = n_0 \exp[-(A+k')t],$$

where A is the transition probability for emission and k' is the specific rate constant for radiationless de-excita-

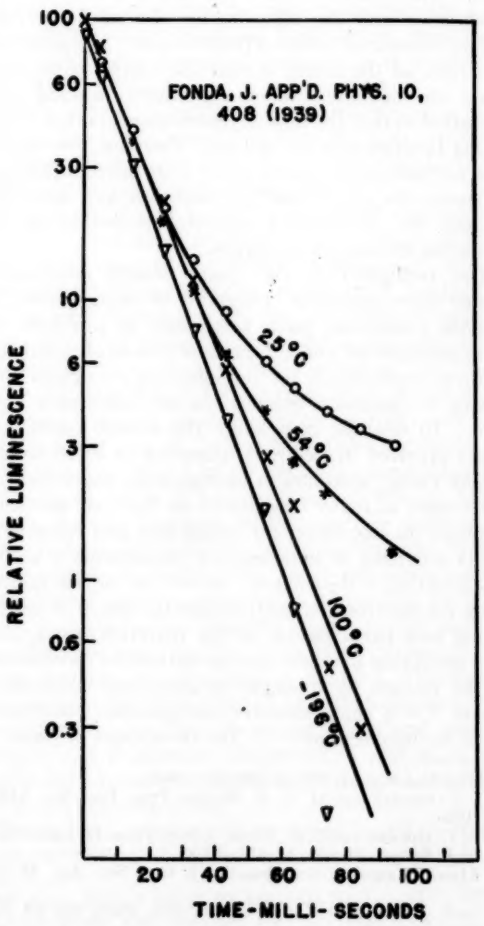

FIG. 5. Experimental evidence for two-stage phosphorescence.

[19] Kröger, Hoogenstaaten, Bottema, and Botden, Physica 14, 81 (1948).

tion and is of the form:[20]

$$k' = se^{-\epsilon/kT}.$$

The emission intensity during phosphorescence is proportional to the product of the transition probability for emission and the number of centers remaining excited:

$$I = \alpha A n = \alpha A n_0 \exp[-(A+k')t] = I_0 \exp[-(A+se^{-\epsilon/kT})t]. \quad (1)$$

From (1) it can be seen that the decay constant should be independent of temperature up to a critical temperature above which it should increase rapidly. This is shown in Fig. 3 for willemite.

Gurney and Mott[15] earlier recognized that the luminescent efficiency with continuous excitation should be proportional to the ratio of the transition probability for emission to the sum of the probabilities for all mechanisms of de-excitation:

$$\eta = p \cdot \frac{A}{A+k'} = p \cdot \frac{1}{1+(s/A)e^{-\epsilon/kT}}. \quad (2)$$

From (1) and (2), it appears that at the same critical temperature at which the decay constant increases the efficiency decreases. This is also shown in Fig. 3.

For phosphors in which electron trapping is important, it is apparent from either Figs. 1 or 2 that thermal activation is pre-requisite for at least part of the emission intensity so that it would be expected that the luminescent efficiency would decrease at low temperatures, especially for phosphors having deep electron traps. The results of the analysis of Williams and Eyring[18] for this effect plus the effect of the activated competing radiationless process are shown and applied to efficiency data for SrS:Sm, Eu on Fig. 4.[21]

B. Two stage afterglow: Fonda[22] has reported phosphorescence measurements on Zn_2SiO_4:Mn at different temperatures with ultraviolet excitation and from these data, reproduced in Fig. 5, has concluded that there are two distinct stages to the afterglow. Referring to Fig. 2 and following the analyses reported by Williams and Eyring,[18] electrons exist in the emitting state and in the electron traps on removing the excitation source. Neglecting the effect of competing radiationless processes the rate of decrease of the concentration of electrons in the emitting state is:

$$-(dn_1/dt) = An_1 - k_2'n_2,$$

whereas the rate of decrease of the concentration of electrons in electron traps is:

$$-(dn_2/dt) = k_2'n_2.$$

The solution of these equations shows two distinct contributions to the phosphorescence, only one being markedly temperature dependent:

$$I = \frac{\alpha A}{(A-k_2')}\{n_{20}k_2' \exp(-k_2't) + [(A-k_2')n_{10} - k_2'n_{20}]e^{-At}\}$$

$$= \beta \exp(-ste^{-\epsilon/kT}) + \gamma e^{-At}. \quad (3)$$

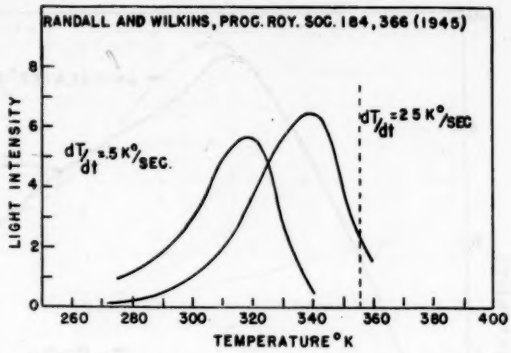

FIG. 6. Theoretical thermoluminescence for a first-order mechanism with no retrapping and no competing radiationless processes, and for electron traps having uniform depth of 0.67 e.v. and frequency factor of 2.9×10^9/sec.

In addition to separating the two stages by temperature changes, the two contributions can be resolved by exciting with different excitation energies so as to excite directly to the emitting state as suggested by Fig. 2.[21,23]

C. Thermoluminescence: Electron trapping is extremely widespread in solids. The thermoluminescent or "glow" experiment is probably the most elegant technique for studying electron traps, so that this is a specific case where the luminescence phenomenon provides a tool for studying an even more general phenomenon. A "glow curve" is obtained by exciting the phosphor, usually at a low temperature; allowing the emission to phosphoresce to a low intensity; and then measuring the emission intensity as the phosphor is heated, preferably at a slow linear rate. Urbach[24] first formulated thermoluminescence, and Randall and Wilkins[9] assuming traps of uniform depth emptying by a first order rate-determining process with no retrapping and neglecting competing radiationless processes deduced the analytic expression for intensity *versus* temperature at constant rate of heating. The rate of decrease in concentration of occupied electron traps is:

$$-(dn/dt) = k_1'n.$$

$$\therefore\ n = n_0 \exp\left[-\int_{t_0}^{t} k'dt\right] = n_0 \exp\left(-\frac{1}{dT/dt}\int_{T_0}^{T} k'dT\right).$$

[20] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).
[21] F. E. Williams, *Solid Luminescent Materials* (John Wiley & Sons, Inc., New York, 1948), p. 337.
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[23] H. W. Leverenz, RCA Review **7**, 199 (1946).
[24] F. Urbach, Wien. Ber. (IIA) **139**, 363 (1930).

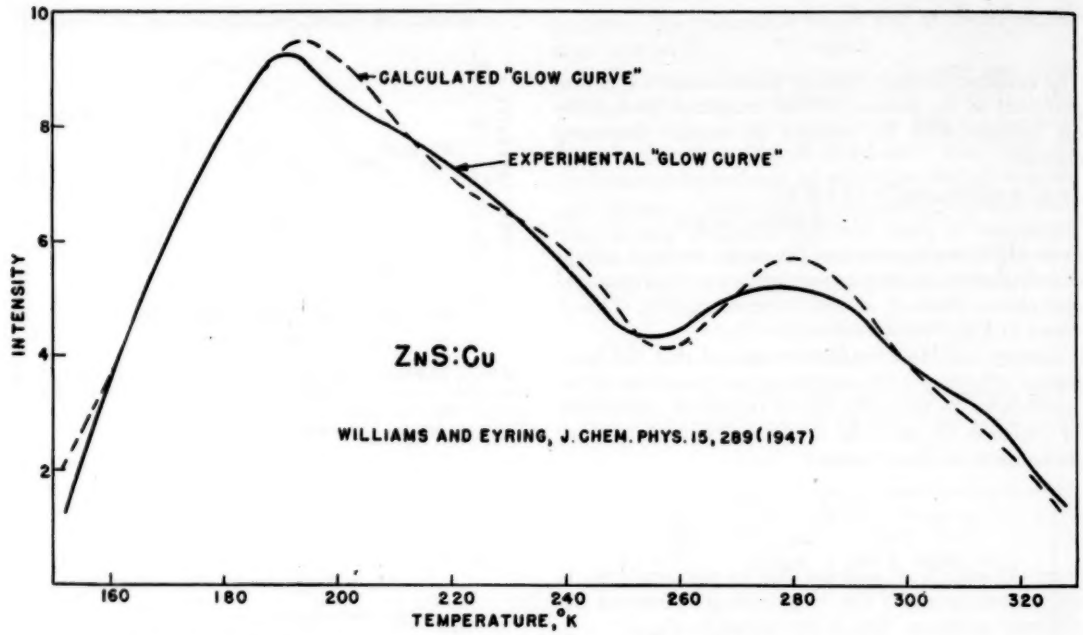

FIG. 7. Comparison of calculated and experimental "glow curves" for complex thermoluminescence.

The emission intensity is as follows and is shown in Fig. 6:

$$I = \alpha k' n = \alpha s e^{-\epsilon/kT} n_0 \exp\left(-\frac{s}{dT/dt}\int_{T_0}^{T} e^{-\epsilon/kT}\right). \quad (4)$$

Williams and Eyring[18] have analyzed complex experimental glow curves obtained at slow rates of heating deriving the explicit expression for the specific rate constants by the following relation:

$$k' = \frac{d}{dT}\left\{\frac{dT}{dt}\left[\sum_{j=1}^{\infty}\frac{1}{j}\left(\frac{\int_{T_0}^{T} I\,dT}{\int_{T_0}^{\infty} I\,dT}\right)^{j}\right]\right\} \quad (5)$$

and have concluded from the shape of glow peaks, the dependence of the glow curve on rate of heating and from theoretical considerations that monomolecular kinetics dominate thermoluminescence in ZnS:Cu. Garlick and Gibson[13] confirm this conclusion from independent evidence. The result of the detailed analysis is shown in Fig. 7. The principal errors of the analyses of thermoluminescence arise from the uncertainty in resolving the individual glow peaks so that too small frequency factors and activation energies are concluded; from neglecting the competing radiationless processes which are appreciably active as evidenced by slightly different light sums being obtained at different heating rates; and from assuming retrapping to be negligible. From the thermoluminescence analysis, the phosphorescence can be computed at any temperature. It is interesting to observe that a relatively uniform distribution of electron traps of different depths result in the t^{-1} afterglow characteristic of sulfide phosphors.[21]

D. Electron retrapping: Recognizing that electron retrapping is probably important in the decay of stimulated brightness and photo-conductivity of infra-red sensitive phosphors, Herman, Meyer, and Hopfield[25] have formulated and obtained general solutions for long-time decay of a system involving electron transfer processes between the conduction band, a discrete set of trapping states, and luminescent centers. Figure 1 is clearly applicable. The electron transfer processes that occur on irradiation with infra-red of intensity I and frequency ν are as follows:

$$dn_0/dt = -An_0n = -(\sigma_L v)n_0 n,$$
$$dn_1/dt = -(\sigma_P I/h\nu)n_1 + (\sigma_T v)[N_1 - n_1]n,$$
$$dn/dt = -(\sigma_L v)n_0 n + (\sigma_P I/h\nu)n_1 - (\sigma_T v)[N_1 - n_1]n,$$

where N_1, n_0, n_1, and n are respectively the concentration of trapping states, empty luminescent centers, occupied trapping states, and electrons in the conduction band; σ_L and σ_T are capture cross sections of the centers and traps for the conduction electrons of velocity v; and σ_P is the infra-red excitation cross section of the trapped electrons. The solution of the above equations predicts that, if there is appreciable re-

[25] Herman, Meyer, and Hopfield, J. Opt. Soc. Am. 38, 1001 (1948).

trapping, then at long times, where retrapping has the greatest effect, the following relations for stimulated brightness and photo-conductivity apply:

$$B \propto [c_1 + c_2 l]^{-2}$$
$$i \propto [c_1 + c_2 l]^{-1}. \quad (6)$$

For ZnS Reimann[26] has reported conductivity and has interpreted brightness data of Antonow-Romanowsky[27] to be in accord with these conclusions. Rigorously the analysis applies only to thin phosphor samples in which the infra-red intensity is constant. By substituting k_1' for the coefficient of n_1 throughout the formulation, the electron transfer occurring with thermal decay is obtained.

E. Positive hole migration: To explain the non-linear dependence of emission intensity I on excitation intensity J at low excitation intensity and the effect of quencher impurities, Klasen and Wise[12,28,29] have developed a theory of positive hole migration. The basic idea can be seen from Fig. 1. Emission depends on the recombination of excited electrons and luminescent centers. However, if the positive holes are thermally activated to the filled band and migrate to a quencher level before recombination can occur, then the luminescent efficiency will be diminished. Because recombination depends on the concentration of excited electrons as well as on the concentration of positive holes in activator states and the migration depends only on the latter, it is obvious that the efficiency will be diminished more at low excitation intensities. The general formulation for n excited electrons and n_i positive holes for the i center is as follows:

$$n = \sum_i n_i$$
$$dn/dt = J \cdot \sum_i \mu_i - n \cdot \sum_i A_i n_i$$
$$dn_i/dt = \mu_i \cdot J - A_i n n_i - k_{if}' n_i + \alpha_{fi}(N_i - n_i) n_f$$

when μ_i is the probability of excitation of the i center, A_i is the recombination probability, k_{if}' is the rate constant for thermal excitation of the positive hole from the i center to the filled band, and α_{fi} is the capture probability of a positive hole from the filled band by an i center containing an electron. An analytic solution has been obtained only for the system consisting of one type of luminescent center from which migration can occur and one type of quencher from which migration cannot:

$$\frac{J}{I_1} = \frac{1}{\mu_1} + \frac{B_1 \exp(-\epsilon_1/kT)}{(\mu_1 I_1)^{\frac{1}{2}}}. \quad (7)$$

The application of the theory to efficiency data on ZnS:Ag, Co is shown in Fig. 8.[12] To correct for the effect of N electron traps of depth ϵ, (7) is modified as follows:

$$\frac{J}{I_1} = \frac{1}{\mu_1} + \frac{B_1 \exp(-\epsilon_1/kT)}{(\mu_1 I_1)^{\frac{1}{2}}} \left(1 + \frac{\alpha N}{\alpha n + s e^{-\epsilon/kT}}\right)^{\frac{1}{2}}.$$

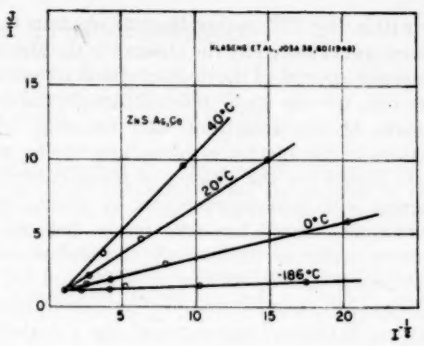

FIG. 8. Application of theory of positive hole migration to intensity dependence of efficiency for phosphor containing one type of luminescence center and one type of quencher.

IV. ATOMISTIC INTERPRETATIONS

The detailed atomistic interpretations of luminescence are in less precise condition than the phenomenological interpretations. However many significant properties of simple ionic phosphors have been qualitatively explained fundamentally.

The thallium-activated alkali-halide phosphors are the most amenable to a fundamental approach because of their simple ionic lattice and the known interaction energies of their constituents.[30] From x-ray measurements and the proportionality of dispersion electrons to thallium content[31] it is known that Tl^+ substitutionally replaces alkali ions. The luminescence transitions

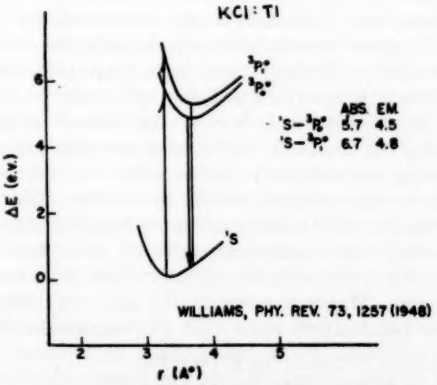

FIG. 9. Calculation of peak absorption-emission energies by computing energy as a function of activator nearest-neighbor distance assuming that the lattice in the region of the activator expands to accommodate the activator in whatever state it exists.

[26] A. L. Reimann, Nature **140**, 501 (1937).
[27] W. W. Antonow-Romanowsky, Physik. Zeits. Sowjetunion **7**, 366 (1935).
[28] H. A. Klasen and M. E. Wise, Nature **158**, 483 (1946).
[29] M. E. Wise and H. A. Klasen, J. Opt. Soc. Am. **38**, 226 (1948).
[30] J. Mayer, J. Chem. Phys. **1**, 270, 327 (1933).
[31] W. Koch, Zeits. f. Physik **57**, 638 (1929) and **59**, 378 (1930).

occur within the Tl^+, rather than as electron transfer processes, as evidenced by the absence in the absorption and emission spectra of the doublet characteristic of the halide ions, by the small temperature-dependence of the peaks of the absorption and emission, by the similarities in the spectra of phosphors having greatly different anions, by the absence of photo-conductivity concurrent with luminescence and by general energy considerations. Seitz[32] has tentatively deduced from qualitative quantum-mechanical considerations that the luminescence involves the $^1S_0-{}^3P_1{}^0$ and $^1S_0-{}^1P_1{}^0$ transitions of the free Tl^+ modified by interactions with the lattice. Williams[33] has reported the calculation of the peak absorption and emission energies of $KCl:Tl$ from a precise configuration coordinate model. For the ground and excited states of the Tl^+, utilizing computed ionic radii and polarizabilities of the excited states, the energy of the system is computed as a function of the activator nearest-neighbor distance with various assumptions as to the behavior of the remainder of the lattice. The Madelung, exchange repulsion, ion-induced dipole and van der Waals interactions are considered in detail. In Fig. 9 are shown the results of the calculation with the assumption that the lattice expands freely to accommodate the activator in whatever state it exists. With this assumption, agreement of the peak energies to within 10 percent of the experimental values is obtained because the ions of the crystal are relatively incompressible compared to the lattice. In order to improve the calculation of peak energies and to permit the calculation of the spectra of absorption and emission, the energy of the system must be computed as a function of the activator nearest-neighbor distance but with the condition that the remainder of the lattice undergoes rearrangements that minimize the total energy. Incidentally, the increased ionic radius of the excited state of the activator is through the repulsion interaction largely responsible for difference in absorption-emission energies; whereas the large polarizability of the excited state increasing the van der Waals interactions and the radial charge density for the excited state beyond the nearest neighbors altering the Coulomb interactions are responsible for reducing the difference between the free ion energy levels so that emission occurs in the near ultraviolet and visible with thallium-activated alkali halides.

Among the manganese-activated phosphors, the $ZnF_2:Mn$ is probably the simplest from the atomistic viewpoint. Magnetic susceptibility and x-ray measurements conclusively show that the manganese in the divalent state is randomly distributed over the cation sites.[34] One of the striking features of manganese-activated phosphors is their long non-temperature dependent exponential phosphorescence. In $ZnF_2:Mn$ the afterglow corresponds to an average lifetime of the emitting state of 0.083 sec.[35] Compared to allowed atomic transition probabilities, it is clear that a strongly forbidden transition is active. Williams and Eyring[18] have attributed the low transition probability to a change in multiplicity, that is, electron spin, accompanying emission; and predicted, therefore, a change in magnetic susceptibility with excitation. This has been confirmed experimentally.[34]

The sulfide phosphors are in the least satisfactory state from the viewpoint of fundamental interpretations. The concurrence of photo-conductivity and luminescence implies that ionization accompanies excitation. From approximate calculations, using close analogy with ZnO, Seitz[36] concluded that the ionization in the pure ZnS does not correspond to the freeing of an electron from the Zn^{++} or $S^{=}$ ions in the lattice, and that neutral interstitial zinc atoms in ZnS and neutral interstitial copper atoms in ZnS:Cu are responsible for the luminescence. Because of the covalent nature of the bonding in sulfides, it is difficult to make precise calculations.

V. CONCLUSIONS

It is apparent that the next phase in the interpretations of luminescence will be precise theoretical calculations on simple phosphors to evaluate quantitatively their significant properties, that is, an absolute theory of luminescence by means of which the magnitudes of properties can be evaluated from first principles. Specific projects for quantitative fundamental interpretations are: (1) the calculation of absorption and emission spectra and their temperature dependence; (2) the precise physical identity of the electron traps responsible for individual glow peaks; (3) a quantitative theory of sensitization; and (4) a detailed theoretical analysis of the efficient transfer of energy from the lattice to the activator observed with electron excitation. With these ideas in mind, it does not seem unduly optimistic to suggest that the interpretations of luminescence phenomena will lead in the not too distant future, not only to increased knowledge of the theory of solids, but also, to the design and improvement of specific phosphors from fundamental considerations.

[32] F. Seitz, J. Chem. Phys. **6**, 150 (1938).
[33] F. E. Williams, Phys. Rev. **73**, 1257 (1948).
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[36] F. Seitz, J. Chem. Phys. **6**, 454 (1938).

Optical Properties of Calcium Silicate Phosphors

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Calcium silicate phosphors activated with varying amounts of manganese luminesce yellow to orange under cathode-ray excitation, but are not excited by ultraviolet λ2537. If a small amount of lead is added with the manganese, the resulting material responds to λ2537 to give the same color as that produced by cathode rays, and in addition to the visible luminescence, there is an ultraviolet band at λ3400. The spectral distribution in the visible is dependent upon manganese concentration and on temperature.

If lead alone is used as an activator, the product gives emission entirely in the ultraviolet. Three emission bands are evident at approximately 3000A, 3340A, and 3500A, any one of which may be predominant, depending upon the conditions of preparation. The excitation spectrum also varies widely, having several maxima between 2000A and 3000A. When the phosphor is excited by 2288A line from a low pressure cadmium arc, a fourth broad band appears in the emission, which peaks about 3850A and extends far enough to the longer wave-lengths to be easily observed visually.

X-ray analysis with a Philips Geiger counter spectrometer demonstrates that the emission band at 3000A is due to the α-metasilicate, the one at 3500A to the β-metasilicate, while the 3340A band is due to the β-orthosilicate. During the firing process the orthosilicate is formed first by the reaction between the calcium oxide and silica in equi-molar proportions, and it reacts thereafter with additional silica to form metasilicate.

CALCIUM silicates which are activated with a few percent of manganese luminesce under cathode-ray excitation, the color varying from yellow to orange as the amount of manganese is increased. These phosphors do not respond to 2537A excitation. If a small amount of lead is added, however, as a second activator, an absorption band is introduced which has its peak in the neighborhood of the 2537A line, and as a consequence this doubly activated material does luminesce when excited by a low pressure mercury arc.[1,2]

The color of the emitted light is the same under ultraviolet excitation as under cathode rays of low current density. As the current density of the cathode rays is increased, a color shift is observed, being most noticeable in the case of the redder samples, which change to yellow with high currents. This has been shown to be due to the temperature increase associated with higher current density, since an identical color shift can be produced in the same phosphors under ultraviolet excitation by placing them on a hot plate. The change in spectral distribution with temperature of two samples containing 5 percent and 1.6 percent MnO, respectively, is shown in Figs. 1 and 2.

The doubly activated material shows, in addition to the visible luminescence due to manganese, a fluorescence in the ultraviolet due to lead, the peak emission being about 3400A.[1] The emission spectra at room temperature of several typical samples under 2537A excitation are given in Fig. 3. The actual brightness as well as the relative intensity of the ultraviolet and visible peaks depends upon the manganese content, but is little affected by the amount of lead. This is not indicated in the curves, since they are all drawn to the same maximum. The shape of the distribution curve in the visible suggests that there are two overlapping bands, one at approximately 5600A and the other between 6100A and 6200A, their relative intensities being determined by the manganese content. The existence of two bands is emphasized in the spectral curves taken at liquid nitrogen temperature, and illustrated in Fig. 1 where the emitted spectrum is given at several temperatures. From these it appears that the longer wave-length peak is emphasized as the temperature is lowered.

When lead alone is used as an activator, the photoluminescence is in the ultraviolet, and the spectral character varies greatly with the method of phosphor preparation. It is dependent also on the wave-length of the exciting light. Under 2537A excitation any one of three emission bands, or a combination of them, may be made to appear depending upon composition and the method of preparation. The nature of these bands is indicated in Fig. 4. These curves were taken with a photo-electric recording spectrometer, and they represent photo-cell response without compensation for the spectral sensitivity of the photo-cathode, or the transmission of the instrument.* They are presented in this way because the correction factor has not been accurately determined below 3300A due to the fact that it is difficult to obtain a source calibrated in this region of the spectrum. The sensitivity of the spectrometer decreases from 4000A to the shorter wave-lengths, being reduced to approximately 50 percent at 3000A. The best data obtained so far indicates that the maxima of Fig. 4 at 3450A, 3340A, and 3000A will all be moved to shorter wave-lengths, approximately 50A, 70A, and 150A, respectively. In this discussion the peaks will be designated according to their positions on the uncompensated records.

Referring again to Fig. 4, the band at 3450A shows the emission of a phosphor, 2935*B*, made by mixing equi-molecular amounts of CaO and SiO_2 with 3 percent PbO. The mixture was fired for six hours at 1000°C in an atmosphere of steam. The band at 3340A was obtained from a phosphor, 2881, made by mixing two moles of CaO and one mole of SiO_2 with 3 percent PbO.

[1] H. C. Froelich, J. Electrochem. Soc. 93, 101 (1948).
[2] J. B. Merrill and J. H. Schulman, J. Opt. Soc. Am. 38, 471 (1948).

* The spectral curves of Fig. 1 in the visible were taken on a prism instrument compensated to give true relative energy.

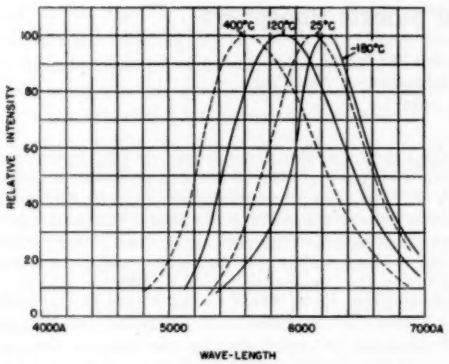

FIG. 1. Variation in emission of $CaSiO_3$:Pb:(5.0 percent) Mn with change in temperature.

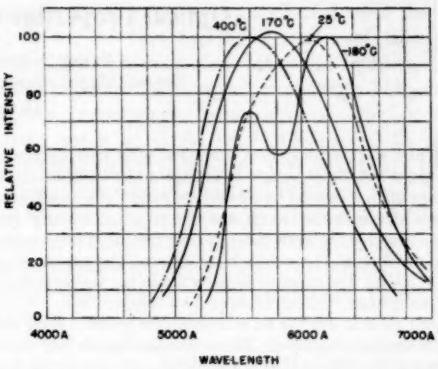

FIG. 2. Variation in emission of $CaSiO_3$:Pb:(1.6 percent) Mn with change in temperature.

The firing was done at 1180°C for one hour in steam. The 3000A band, as in 2862, was characteristic of all phosphors made of equi-molecular parts of CaO and SiO_2 regardless of the amount of PbO, when the firing was carried out at 1180°C in steam. All samples were fired in a platinum boat.

The existence of the three distinct spectrum bands in the different phosphors suggests that different compounds are produced according to the composition used and the method of firing. The number and the identity of the possible compounds has been deduced by E. S. Shepherd and G. A. Rankin[2a] from their thermal diagram. In the temperature zone in which we have been working, lying below 1200°C, there are, in fact, three possible compounds which may exist as stable forms, depending upon the composition involved.

Calcium metasilicate—as α-$CaSiO_3$ stable above 1190°C.
Calcium metasilicate—as β-$CaSiO_3$ stable below 1190°C.
Calcium orthosilicate—as β-Ca_2SiO_4 stable below 1430°C.

The thermal diagram is a guide which shows what compounds are to be expected if the reaction does, in fact, go to completion. At the temperature involved in the preparation of the phosphor, there is always the possibility that some constituents of the mixture may remain in an unreacted form, and that the aggregate formed between them and the reacted compound may determine the luminescent character of the resulting phosphor. In order, therefore, to identify the actual composition of a phosphor, reliance was placed upon the x-ray diffraction pattern. Graphs of such patterns were recorded with the North American Philips Geiger counter x-ray spectrometer. They are in reasonable agreement with the data recorded by Hanawalt, Rinn, and Frevel[3] for α-$CaSiO_3$, β-Ca_2SiO_4, and CaO, and by Ehrenberg[4] for β-$CaSiO_3$.

From these results it appears that different compounds result from different compositions and from different methods of preparation, and the spectrum of the fluorescence varies accordingly. The 3000A band is associated with the α-metasilicate (α-$CaSiO_3$), the 3450A band with β-metasilicate (β-$CaSiO_3$), and the 3340A band with β-orthosilicate (β-Ca_2SiO_4). Table I gives the relative intensities of the emission bands for a group of typical phosphors. Excitation maxima are also given in this table, and will be discussed later.

When manganese is present as well as lead, the location of the ultraviolet emission band depends upon the concentration of manganese. This is not due to the introduction of an independent Mn band in the ultraviolet but rather to the effect of manganese in raising the transition temperature between the α- and β-forms of $CaSiO_3$, an effect which increases with manganese concentration.[5] The bearing of this effect upon the yellow and orange emission bands of manganese has already been described.[6] The variations in locations of the ultraviolet lead emission bands are shown in Table II. All phosphors had been prepared from mixtures containing 3 percent PbO.

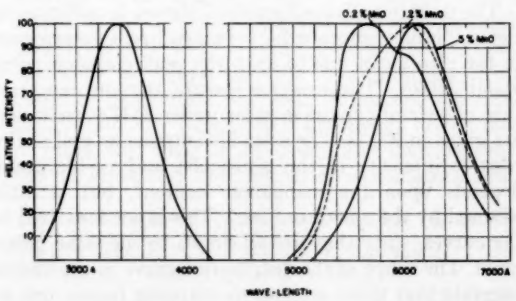

FIG. 3. Dependence of emission spectra of $CaSiO_3$:Pb:Mn upon concentration of manganese. Measurements made at room temperature.

[2a] E. S. Shepherd and G. A. Rankin, Zeits. f. anorg. allgem. Chemie **71**, 19 (1911).
[3] Hanawalt, Rinn, and Frevel, Ind. Eng. Chem., Anal. Ed. **10**, 457 (1938).
[4] H. Ehrenberg, Zeits. f. physik. Chemie **B14**, 425 (1931).
[5] E. Voos, Zeits. f. anorg. allgem. Chemie **222**, 201 (1935).
[6] G. R. Fonda and H. C. Froelich, J. Electrochem. Soc. **93**, 114 (1948).

TABLE I. Dependence of emission and excitation bands on constitution.

Compound	No.	Firing temp.	Excitation 2300	2600	2800	3000	Emission 3340	3450A	3600
α-$CaSiO_3$(3)Pb	2862*A*	1180°	100			12			
β-$CaSiO_3$(3)Pb	2935*B*	1000°	45	100				92	
β-$CaSiO_3$(3)Pb(1)Mn	2842	1180°	82	100		6		24	
β-Ca_2SiO_4(3)Pb	2881	1180°	37	100	60	10	83		
CaO(1)Pb	2925*B*	1180°	16	28	100				25

In addition to the change in the spectral location of the Pb emission band, an effect which is due primarily to the change in structure, the manganese reduces the intensity of the Pb emission. This effect upon the emission of an activator is always apt to occur in the presence of another activator, particularly when the emission of the latter, manganese in this case, lies at a longer wave-length. The excitation energy is shared between the two activators.

When phosphors are prepared from mixtures that do not conform to stoichiometric proportions, no new emission bands appear but simply combinations of the bands listed in Table I. This is particularly clear in the case of phosphors prepared from mixtures of more than one mole of CaO per mole SiO_2. As shown by their diffraction patterns, the orthosilicate, β-Ca_2SiO_4, begins to form as soon as the mole ratio of CaO to SiO_2 exceeds unity; furthermore, free CaO is formed when the proportions for the orthosilicate are exceeded. The correlation between composition and structure, on the one hand, and emission, on the other, is given in Table III. All phosphors were prepared at 1180° from mixtures with 3 percent PbO with the exception of 2925B, which contained 1 percent PbO.

When phosphors were prepared from mixtures containing more SiO_2 than corresponded to metasilicate proportions of 1 mole CaO to 1 mole SiO_2, the emission was considerably reduced but the 3340A as well as the 3000A band appeared. Although the 3340A emission band corresponds normally to β-Ca_2SiO_4, it is evident from the recorded curves of diffraction patterns that the only calcium compound present is α-$CaSiO_3$. The 3340A band must therefore be ascribed to an aggregate, α-$CaSiO_3 \cdot SiO_2$. A summary of the results is given in Table IV for phosphors prepared with 3 percent PbO at 1180°C.

When the firing of a mixture in metasilicate proportions was carried out at 1180° in air rather than in steam, the emission of the resulting phosphor appeared at first to be anomalous. Its position was at 3340A rather than at 3000A. Examination of its diffraction pattern disclosed the reason. In its constitution, it proved to be not α-$CaSiO_3$ alone but to contain, in addition to this form, some β-Ca_2SiO_4 and some SiO_2 as cristobalite, with no evidence of free CaO. From Tables III and IV it is evident that the presence of either of these products, β-Ca_2SiO_4 or α-$CaSiO_3 \cdot SiO_2$, would give rise to the 3340A emission band.

The reaction is known to progress more sluggishly in air, so that it affords an opportunity to segregate any intermediate products that might be formed as a first step of the reaction. The results just described are therefore of particular interest in demonstrating what has been observed previously, that Ca_2SiO_4 is the product formed first by the reaction between CaO and SiO_2 in equi-molar proportions and that it reacts thereafter with additional SiO_2 to form $CaSiO_3$. Wherever Ca_2SiO_4 remains in the final product, there must of course also be some free, unreacted SiO_2.

The initial formation of calcium orthosilicate in the reaction between calcium oxide and silica was confirmed by short firings at 1180° in steam. After a two-minute firing, too short to allow completion of the reaction, a diffraction pattern of the mixture showed prominently the lines of the orthosilicate, β-Ca_2SiO_4, as well as of the metasilicate, α-$CaSiO_3$, and of unreacted CaO. After a five-minute firing, the lines of cristobalite appeared as well, denoting a rather slow crystallization of the precipitated silica employed. Only on prolonged firing was the pattern altogether that of α-$CaSiO_3$.

Because of its short wave-length emission, as low as 3000A, the α-$CaSiO_3$·Pb is of particular interest and the dependence of emission intensity upon lead content was investigated. As shown in Table V, there is an optimum point for phosphors prepared with about 6 percent PbO.

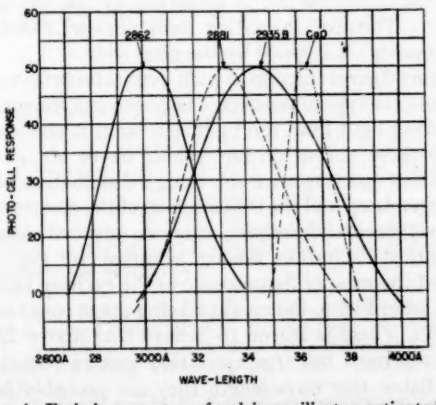

FIG. 4. Emission spectra of calcium silicates activated with lead as dependent upon composition and structure—2935*B*—β-$CaSiO_3$:Pb; 2862—α-$CaSiO_3$:Pb; 2881—β-Ca_2SiO_4:Pb.

TABLE II. Dependence of ultraviolet lead emission of $CaSiO_3$ upon manganese content.

No.	% Mn	Firing temp.	Structure	Emission intensity 3000A	3450A
2862*A*	0	1180°	α	12	
2858	0.05	1180°	α	12	6
2857	0.10	1180°	α+little β	10	9
2856	0.20	1180°	α and β	7	25
2842	1.00	1180°	β+little α	6	24
2864	2.00	1180°	β	2	7
2865	3.00	1180°	β	2	5
2935*B*	0	1000°	β		92

TABLE III. Emission of phosphors of composition $(1+n)$ $CaO \cdot SiO_2 \cdot Pb$.

No.	Mole CaO	Mole SiO_2	Structure	Emission intensity 3000A	3340A	3600A
2862A	1.00	1.00	α-$CaSiO_3$	12		
2944	1.25	1.00	β-Ca_3SiO_4+3α-$CaSiO_3$	22	34	
2943	1.50	1.00	β-Ca_3SiO_4+α-$CaSiO_3$	20	83	
2881	2.00	1.00	β-Ca_2SiO_4	10	83	
2929	4.00	1.00	2CaO+β-Ca_2SiO_4	4	29	28
2928	10.00	1.00	8CaO+β-Ca_2SiO_4		4	26
2925B	1.00	0	CaO			25

ABSORPTION AND EXCITATION SPECTRA

The absorption characteristics of the phosphors from 2000A to 3000A were studied by measuring the reflection of a plaque of the powder 1 mm thick, with respect to a similar plaque of smoked magnesium oxide. The series of samples to be compared were mounted in a circular metal plate which could be conveniently and accurately rotated in such a way as to bring them successively into a given position in front of the spectroscope slit. A hot-cathode hydrogen lamp was used as a source since this gives a continuous spectrum to 2000A or lower. The spectrum of the reflected light was taken with the recording spectrometer, which requires less than a minute to cover the spectral range from 2000A to 3000A.

The variation in the reflectivity with wave-length of typical samples is shown in Fig. 5, which gives percent reflection referred to magnesium oxide smoked on a pressed MgO surface.

The excitation spectra of the phosphors were investigated by painting a thin layer on a small glass slide which could be mounted at the exit-slit of the spectrometer directly in front of the photo-multiplier, the phosphor being on the side of the glass away from the photo-cell. With this arrangement, as the cell sweeps through the spectrum of the hydrogen lamp, the phosphor is progressively excited by different wave-lengths, and the resulting luminescence is indicated by the photo-cell output. The direct exciting light (below 3000A approximately) is stopped by the glass slide.

Figure 6 gives tracings of such "excitation curves" for a number of typical samples. The photo-cell response for the direct light from the hydrogen lamp is also shown. While these curves do not enable us to obtain true excitation spectra, since the energy distribution of the hydrogen lamp and the transmission of the spectrometer has not been determined, they do give a basis for comparing excitation among samples. In Fig. 7 is plotted the ratio of fluorescence to the exciting light, as taken from Fig. 6, the maxima being made equal for all samples. There is reason to believe that above 2200A these represent the true excitation spectra reasonably well. Below this wave-length they are probably badly distorted, due primarily to the absorption of the photo-cell envelope in this region. This would cause the readings for the exciting energy to be too low, while the response due to the fluorescent light would be unaffected.

The excitation spectra appear to be complex, consisting of several peaks, whose relative prominence depends upon the particular crystal phase which is developed in the process of preparation. The α-metasilicate has associated with it an excitation band around 2300A. The β-metasilicate shows a relatively much stronger peak at 2600A. The β-orthosilicate excitation is similar to the β-metasilicate, except that the 2600A band is broader and displaced slightly to shorter wave-lengths. On the original records excitation maxima for several of the phosphors may be noted at 2100A and below.

Comparison of the reflection curves with the excitation curves shows, as would be expected, a general correlation between absorption and excitation. For example, No. 2862A (α-$CaSiO_3$) shows low reflection at 2300A where strong excitation occurs. Similarly the No. 2935*B* (β-$CaSiO_3$) and No. 2881 (β-Ca_2SiO_4), which show strong excitation at 2600–2700A show low reflection in this region.

In view of the complex excitation and emission spectra, it might be anticipated that the region of excitation would affect the spectral distribution of the emitted light. To test this, for the phosphor 2862A (α-$CaSiO_3$), a cadmium low pressure arc was used, with a strong resonance line at 2288A. Under this excitation it is surprising to find that in addition to those previously observed, an entirely new broad emission band appears with its peak about 3850A, extending far enough to the longer wave-lengths for its presence to be

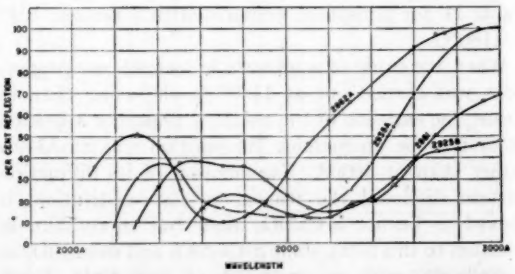

FIG. 5. Reflectivity of calcium silicate phosphors activated with lead as dependent upon composition and structure—2935*A*—β-$CaSiO_3$:Pb; 2862*A*—α-$CaSiO_3$:Pb; 2881—β-Ca_2SiO_4:Pb; 2925*B*—CaO:Pb.

TABLE IV. Emission of phosphors of composition $CaO\cdot(1+n)SiO_2\cdot Pb$.

No.	Mole CaO	Mole SiO_2	Structure	Emission intensity 3000A	3340A
2862A	1.00	1.00	α-$CaSiO_4$	12	
2948	1.00	1.10	α-$CaSiO_4$+0.10 SiO_2	4	4
2947	1.00	1.25	α-$CaSiO_4$+0.25 SiO_2	5	5
2946	1.00	1.50	α-$CaSiO_4$+0.50 SiO_2	3	4
2880	1.00	2.00	α-$CaSiO_4$+1.00 SiO_2	3	6

TABLE V. Dependence of emission intensity on lead content in α-$CaSiO_3\cdot Pb$.

No.	% PbO	Intensity of 3000A band
2877	1	6
2862A	3	12
2878	6	23
2867	10	21
2879	20	1

easily observed visually. This band was of relatively high intensity as will be observed in the curves of Fig. 8. An obvious assumption to account for this new band is that there is in the phosphor a component which responds to 2288A but not to 2537A. There is, however, no evidence in the x-ray diffraction patterns to indicate that such a component is present in the phosphor. The possibility was also considered that a product such as would be formed by firing CaO and SiO_2 without an activator might be responsible for the 3850A band, but when this was tried no luminescence was found in the material.

DISCUSSION

Our observations on the calcium silicate phosphors disclose that they illustrate three different aspects of luminescence. In the first place, there is the dependence of the spectral location of the emission upon the structure of the silicate, as observed for the phosphors activated by lead. This is not surprising. The spectral location of the emission band associated with any activator always varies more or less, depending upon the basic compound in which the activator is incorporated. This is the result of changes in the distribution of internal energy which modulate the energy levels responsible for luminescence. It is to be expected that a change in structure would have a similar effect. In fact, previous instances of it have been observed, such as for the two forms of zinc sulfide.[7]

There is another aspect, however, which is more unusual. The excitation spectrum of α-$CaSiO_3$:Pb shows three excitation bands, at 2100A, 2330A, and 2550A. Under 2537A excitation, the emission comprises simply one band with a peak at 3000A. Under 2288A, on the other hand, this emission band becomes relatively weak and a new predominant band appears at 3850A. No evidence could be found for the presence of a second component, of different structure or composition. A similar effect has been observed previously in the cases of calcium tungstates activated with bismuth.[8,9] This additional example emphasizes the need for elucidation.

The results bear a partial similarity to those described by Kröger for tungstate phosphors of the alkaline earths, activated by lead.[10] In these tungstates, the long wave-length edge of the absorption band, normally at about 2500A, was extended to longer wave-length by increase in concentration of lead. Excitation by 2537A gave invariably a blue emission, regardless of the lead content, in a band whose peak lay in the range 4000–4500A. Excitation by 3130A, on the other hand, gave a green emission for those phosphors containing so much lead that their absorption band had been extended to include 3130A. The peak of this green band lay in the range 5100–5600A. The blue band was no longer noticeable under 3130A excitation. This situation was most clearly shown at −180°C but it was observable also at 25°C. There is this in common between Kröger's tungstates and our silicates both activated with lead, that a separate emission band becomes predominant when the excitation is changed from one absorption band to another.

There is a third feature of our tests which is particularly noteworthy because it furnishes further evidence in support of a recent hypothesis that the position of the emission band may be dependent on the degree of association of the activator ions. It concerns the double band emission which has been observed with certain individual activators, such as manganese, lead, and thallium.[11] The shorter wave-length band is associated with low concentration of the activator and the longer band, with high concentration. One of the phosphors showing it is the $CaSiO_3$:Mn:Pb of our tests.

We have confirmed the presence in its emission of two bands, whose relative intensity is dependent on the

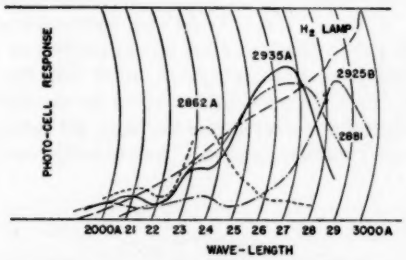

FIG. 6. Excitation curves, as recorded, for the calcium silicate phosphors of Fig. 5 activated with lead, as dependent upon composition and structure.

[7] G. R. Fonda, Trans. Electrochem. Soc. 87, 339 (1945).

[8] Servigne, Bull. Soc. Franc. Mineral 62, 262–80 (1939).

[9] McKeag and Ranby, USP, 2, 257, 699 (Sept. 30, 1941).

[10] F. A. Kröger, *Some Aspects of the Luminescence of Solids* (Elsevier Publishing Company, Inc., New York, 1948), pp. 120–132.

[11] G. R. Fonda and H. C. Froelich, *Preparation and Characteristics of Solid Luminescent Materials* (John Wiley & Sons, Inc., New York, 1948).

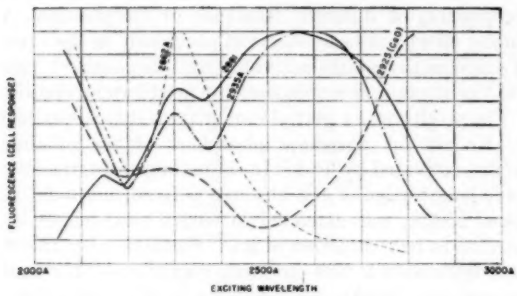

FIG. 7. Excitation curves of Fig. 6 expressed as the ratio of fluorescence brightness to the intensity of the exciting radiation.

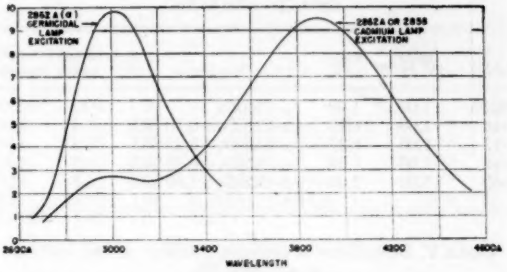

FIG. 8. Emission spectra of calcium silicate phosphors activated with lead as dependent on excitation by 2537A (germicidal lamp) and by 2288A (cadmium lamp)—2862*A*—α-$CaSiO_3$: Pb.

manganese concentration. We have now also shown that an increase in temperature favors the shorter wave band. This observation gives added significance to results on phosphors, previously studied, which showed, in addition to the double band emission, the same behavior on increase in temperature, zinc beryllium silicate[12] and zinc silicate,[13] both activated with manganese.

Maurer has pointed out that the occurrence of double band emission may be explained by assuming that the long wave-length band is due to the presence of pairs of activator ions whereas the short wave-length band is due to single ions.[14] An increase in activator concentration will favor the formation of pairs. From the same viewpoint, an increase in temperature will favor the formation of single ions and therefore produce the accentuation of the shorter wave-length band that has been observed in these three phosphors. Maurer's explanation seems worthy, therefore, of serious consideration.

It should be noted that the same temperature effect has been observed in the self-activated phosphor, $MgWO_4$. At any specific temperature it appears to have one band only, but the position of its peak is shifted to shorter wave-length by increase in temperature.[15] The band is so broad that it may, in fact, be made up of two bands. From another viewpoint, we are accumulating evidence which tends to support this view.

We would like to express our appreciation to E. T. Asp of this laboratory for providing us with the x-ray diffraction patterns.

[12] F. J. Studer and L. Gaus, *Preparation and Characteristics of Solid Luminescent Materials* (John Wiley & Sons, Inc., New York, 1948).
[13] F. A. Kröger, Physics **6**, 764 (1939).
[14] R. V. Maurer, *Preparation and Characteristics of Solid Luminescent Materials* (John Wiley & Sons, Inc., New York, 1948).
[15] See reference 12, p. 263.

The Luminescence of Zinc Sulfide Activated by Lead

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Zinc sulfide activated by lead shows fluorescence in various bands, two of which can be attributed to lead. The first band has a maximum at 4850A, the second one at 6100A. The orange band is favored by sulfurizing conditions and appears irrespective of whether halide ions are present or not. This band is attributed to a characteristic electronic transition in divalent lead ions, occupying normal lattice sites. The green band is favored by reducing conditions and only appears when chlorine ions are present. This band is attributed to electron transfer transitions between positive and negative ions of configurations formed by monovalent lead and chlorine ions, situated at normal lattice sites, together with the neighboring lattice ions. A green band appearing in reduced zinc sulfide is attributed to a stoichiometric excess of zinc.

INTRODUCTION

FLUORESCENT zinc sulfide containing lead as an activator was first prepared by Lenard,[1] who observed fluorescence in bands at 4555, 5000, and 5850A. There is little doubt that the first band is that of self-activated ZnS[2] but the other bands seemed to be due to lead. Tiede and Weiss,[3] however, were unable to reproduce their results; they concluded that, in accordance with their rule of atomic radii, the lead atom was too large to be incorporated in ZnS, and Riehl,[4] using radioactive isotopes, has given further proof for this view. Therefore, it seemed that the bands found by Lenard should be ascribed to contaminations like copper and manganese.

A few years later, however, Fonda[5] rediscovered the activating properties of lead in ZnS in a search for infra-red sensitive phosphors. Lead was found to cause two bands with maxima at 4900 and 5800A very close to those reported by Lenard. Fonda prepared his samples from ZnS with the addition of as much as 5 percent of $PbSO_4$ or other lead compounds with NaCl as a flux and fired in nitrogen. Since lead compounds are very volatile, only a small fraction of the lead first added is retained in the product.*

The proportion in which the green and orange bands of ZnS—Pb are formed, or, in other words the proportion of "green" and "orange" centers, depends on the conditions of preparation. According to Fonda, the green band is favored by heating in N_2 while the orange band is favored by a high concentration of lead.

It is the purpose of our present work to study further the conditions under which green and orange centers are formed. On the basis of our results we shall try to arrive at a model for these centers.

[1] P. Lenard, *Handbuch der Experimentalphysik* (Akademische Verlagsgesellschaft, Leipzig, Germany, 1928), Vol. XXIII, p. 397.
[2] F. A. Kröger and J. E. Hellingman, J. Electrochem. Soc. **93**, 156 (1948).
[3] E. Tiede and E. Weiss, Ber. **65**, 364 (1932).
[4] N. Riehl and H. Ortmann, Zeits. f. physik. Chemie **A188**, 109 (1941). N. Riehl, Trans. Faraday Soc. **35**, 138 (1938).
[5] G. R. Fonda, J. Opt. Soc. Am. **36**, 382 (1946).
* This is probably the explanation of the negative results of the German investigators.

EXPERIMENTAL

In order to prevent the evaporation of the lead we have prepared our samples in sealed quartz tubes.

First we investigated the influence of the concentration of lead. We used a pure ZnS made by Orr (England), which contained an appreciable amount of chlorine ($\sim 2.5 \cdot 10^{-2}$ at Cl/mole). This ZnS was activated with 10^{-7}, 10^{-6}, 10^{-5}, 10^{-4}, $2.5 \cdot 10^{-3}$, and $4 \cdot 10^{-2}$ gram atoms Pb/mole Zns added as a solution of $Pb(NO_3)_2$ in water. Small quartz tubes were filled with these preparations and the air was driven off by H_2S. Then the temperature was raised to 500°C in order to transform the nitrate into sulfide and to remove adsorbed gases. The pressure of the H_2S was then lowered to ~ 1 cm of Hg and the tubes were sealed off. They were fired for half an hour at 1150°C. All preparations showed the orange lead emission when excited by a suitable radiation (ultraviolet $\lambda = 3655$A), the intensity increasing with increasing concentrations of lead. Products with low contents of lead, in addition, show the blue band due to self-activation (Fig. 1). Products with the highest amount of lead ($4 \cdot 10^{-2}$) were greyish, due to PbS present as a separate phase. Infra-red sensitivity could not be detected. At low temperatures the orange band becomes deep red (Fig. 3, d, e).

In a second series the activator was added as lead metal and the tubes were filled with nitrogen. The concentrations of metal added were 10^{-3} and $5 \cdot 10^{-2}$ gram atoms, Pb/mole. All samples fired under these reducing conditions showed a strong sensitivity to infra-

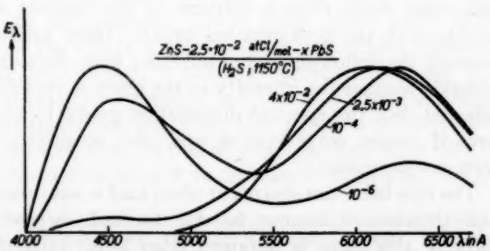

FIG. 1. Spectral distribution of the fluorescence of ZnS containing chloride heated with various amounts of PbS in an atmosphere of H_2S at 1150°C (sealed tubes). Excitation by $\lambda = 3650$A.

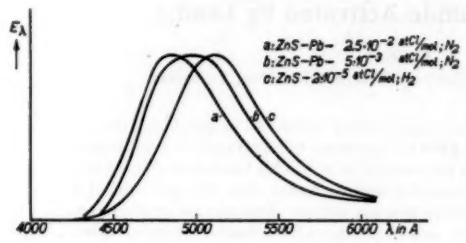

FIG. 2. Spectral distributions of the fluorescence of ZnS containing various amounts of chloride after firing in closed tubes in the presence of lead metal (a, b) compared with that of pure chloride free ZnS, heated in hydrogen (c). Excitation by $\lambda = 3650$A.

red with emission in the green band. After the firing, part of the lead metal remained free and was deposited on the walls of the tube.

So far we always used a ZnS containing chloride. In view of the specific effects of chlorine ions on the fluorescence of other bands (ZnS—Zn, —Ag, —Cu, Rothschild,[6] Kroeger and Hellingman[2]) it seemed worth while to investigate whether such an effect is also found with lead. We therefore dechlorinated our ZnS by heating in a current of H_2 at 1050°C until the blue fluorescence had disappeared, which was the case after about 10 hours. In order to remove a possible excess of Zn the sulfide was heated afterwards for 1 hour in a current of H_2S. Analysis showed that the sulfide contained about $2\cdot10^{-5}$ gram atoms Cl/mole.

Products with the dechlorinated zinc sulfide fired with lead metal in nitrogen showed emission in the orange and green bands, but the relative intensities fluctuated. A study of the spectral distribution showed that the maximum of the green emission had shifted over ~150A toward longer wave-lengths with respect to that found in the chlorinated samples (Fig. 2, a, b). Since all products had the same crystal structure (wurzite) this difference cannot be explained by a difference between wurtzite and sphalerite[2] but must be due to the appearance of a new band with a maximum near 5100A. The different characteristics of this material are also indicated by the fact that these products are very little sensitive for infra-red.

Products with intermediate concentrations of chloride were made from a mixture of the original zinc sulfide with the dechlorinated sulfide. These products showed the following characteristics: with decreasing chloride content the intensity in the green is very little affected, but the spectral distribution gradually shifts toward longer wave-lengths and the sensitivity to infra-red decreases.

The new band can also occur when lead is not present, and therefore it cannot be due to lead. A product showing this band is obtained from pure halide-free ZnS by the following treatments: (a) heating in hydrogen (Fig. 2, c), (b) heating in a sealed tube containing zinc metal.

When the green fluorescent product obtained in (a) or (b) is heated together with a chloride or in an atmosphere of H_2S—HCl, the green fluorescence is replaced by the blue band of ZnS—ZnCl. We therefore believe that the green fluorescence with a maximum at ~5150A is due to an excess of zinc, just as is the case with ZnO.

Accordingly, in a sulfurizing atmosphere and in the presence of chlorine this disturbing band will not occur. As we have seen from our second series, chlorine favors the green lead band. It must therefore be possible to make products with a varying amount of green and orange lead centers without the complication of green zinc centers by carefully balancing sulfurizing and chlorinating conditions. This indeed proved to be the case.

The experiment was carried out by heating ZnS containing chloride with the addition of various amounts of sulfur in a sealed tube in nitrogen, the temperature not being raised above 120°C before sealing off. In the presence of about $2.5\cdot10^{-2}$ gram atoms Cl/mole, the addition of even relatively large amounts of sulfur did not cause a marked increase of the orange band. With a sulfide containing about $5\cdot10^{-3}$ gram atoms Cl/mole, however, the orange band increases with increasing sulfur content as may be seen in Fig. 3, a, b, c.

When CdS is incorporated in ZnS—Pb the orange band remains practically unaltered, but the green band is displaced toward longer wave-lengths, as is known for bands of Ag, Cu, and others. The green band must therefore be a transfer band in which electrons are brought from one kind of ion to another. The orange band, on the other hand, must be a characteristic band, due to electronic transitions within the lead ions, as is the case with ZnS—Mn. In accordance with this view lead also causes a red fluorescence in CaS and SrS.

From the fact that the orange band is favored by a sulfurizing atmosphere while chlorine is unnecessary, we conclude that the orange centers are formed by

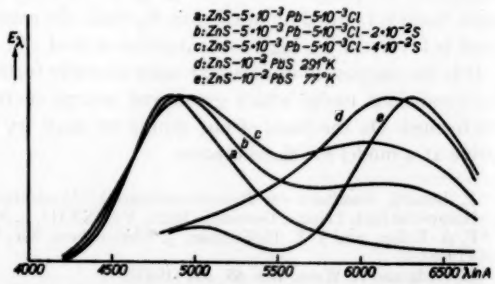

FIG. 3. Spectral distributions of the fluorescence of ZnS-Pb containing chloride prepared in sealed tubes with addition of various amounts of sulfur (a, b, c). Curves d and e show spectral distributions of the orange lead band at room temperature and at the temperature of liquid air.

[6] S. Rothschild, Trans. Faraday Soc. 42, 635 (1946).

Pb^{2+} occupying Zn^{2+} sites; we are dealing with normal ZnS–PbS mixed crystals.

The green band, on the other hand, is found when chloride is present and is favored by reducing conditions. In analogy to what has been assumed for the blue centers in ZnS, we believe that the green Pb centers consist of the monovalent ions Pb^{+} and Cl^{-} occupying normal lattice sites. Just as with these blue centers, it is still open to question whether the actual level is caused by the configuration in which Pb^{+} and Cl^{-} occupy neighboring sites or in which they are far away from each other ($Pb^{+}Cl^{-}$ dissociated).

The Pb^{+} ion appears to be very large in relation to the ions of the ZnS lattice, so that the assumption of incorporation of this ion seems unreasonable. There are, however, several reasons justifying this assumption.

In the first place, the binding between a Pb^{+} ion and the surrounding S^{--} ions (or S^{--} and Cl^{-}) will have a covalent character, resulting in a decrease of the effective ionic radius.

In the second place, the monovalent ion in the lattice built up of divalent ions constitutes a missing charge which will cause an outward displacement of the surrounding lattice ions.[7]

On the other hand, Van der Waals' forces and electron polarization of the lattice round the missing charges increase the attraction between the monovalent ions and the surroundings and therefore lower the energy of our configuration. When Pb^{+} and Cl^{-} are situated on neighboring sites the latter effects are much smaller but a reciprocal polarization of the two ions appears instead.

[7] R. W. Gurney and N. F. Mott, *Electronic Processes in Crystals*, (Oxford University Press, New York, 1940), p. 61.

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The Emission Characteristics of Fluorescent Pigments

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Emission spectra are shown for five pigments whose fluorescent colors are: blue, green, yellow, orange, and red. These are compared to reflectance spectra of paints tinted to approximate, in daylight, the fluorescent colors of the five pigments and to a series of standard artist's colors. The paper attempts to bring up to date practical information on the production of brightness with these phosphors. Following the general lines of development used by Kraehenbuehl and Chanon, data are given showing the relation between ultraviolet intensity and fluorescent brightness and between the latter and the masking effect of ambient illumination. The efficiency of light production from fluorescence excited by different types of commercial sources of near ultraviolet is described.

INTRODUCTION

THE incorporation of a light source into a medium such as paint, plastic, or textile in the form of fluorescence presents possibilities for illumination and design limited only by the imagination. Data on the use of near-ultraviolet radiation for the production of visible light have been published[1] but there is a need to extend this information and bring it up to date. This paper considers the properties and performance of certain fluorescent materials from the viewpoint of their usefulness as illuminants.

MATERIALS

The discussion is limited to materials which are excited to fluorescence by radiation between 3200 and 4000 Angstrom units. This range of the ultraviolet spectrum, popularly known as black light, is of longer wave-length than the ultraviolet which is harmful to the eyes and can be used with safety[2] for illumination of fluorescent materials. The pigments themselves contain no radioactive material and are no more toxic than some of the pigments which are widely used in paints.[3]

Although pigments can be prepared which fluoresce in an unlimited variety of colors, this discussion deals primarily with only five of the commercially available pigments. As shown in Table I, the fluorescent colors of the five pigments (2205, 2210, 2215, 2220, 2225) cover the visible spectrum quite well. These pigments may be blended to produce intermediate hues. For most satisfactory results it is best to obtain the desired color from mixtures of the two pigments adjacent to it in the spectrum. In this way intermediate hues may be obtained with little or no decrease in fluorescent bright-

[1] J. O. Kraehenbuehl and H. J. Chanon, Trans. I. E. S. **36**, 151 (1941).

[2] Matthew Luckiesh, *Applications of Germicidal, Erythemal, and Infra-Red Energy* (D. Van Nostrand Company, Inc., New York, 1946), Chapter XIII.

[3] *The ABC of Luminescence* (The New Jersey Zinc Company, New York, 1944), p. 16.

TABLE I. Characteristics of fluorescent pigments.

Pigment No.	Composition	Daylight color	Fluorescent color	Tinting pigment required*
2100	ZnO/Zn	White	Light green	—
2200	ZnS/AgCu	White	Blue white	—
2205	ZnS/Ag	Near white	Purple blue	10 percent cobalt blue
2210	ZnS/Cu	Pale yellow green	Green yellow-green	0.3 percent phthalocyanine green plus 0.7 percent zinc yellow
2215	80 ZnS / 20 CdS / Cu	Cream	Yellow	2 percent Hansa yellow
2220	70 ZnS / 30 CdS / Cu	Buff	Yellow red	1.3 percent dinitroaniline orange
2225	50 ZnS / 50 CdS / Cu	Orange brown	Red-yellow red	2.6 percent toluidine toner

* To produce similar daylight and fluorescent color.

ness over that to be anticipated from the brightness of the constituents. This rule does not hold, however, in mixing to produce white fluorescence.

The color of these fluorescent pigments in daylight or artificial illumination varies from white to tan. In order to make fabricated articles more attractive, it is sometimes desirable to add regular coloring pigments along with the fluorescent pigments. Such additions of pigment which produce color by absorption naturally reduce the amount of light emitted from the fluorescent material but by proper selection of tinting materials it is possible to prepare paints of attractive color under both daylight and black light illumination. Less reduction in emission results if one selects, for a tint base, the pigment whose fluorescent color most closely approximates the desired daylight color. This gives higher fluorescent brightness than would be obtained by tinting a white fluorescent paint with a colored pigment. Recommendations for tinting fluorescent pigments to produce similar daylight and fluorescent colors are given in Table I. For some purposes it may be desirable to design materials which differ in color under black light and daylight illumination, and, while this is possible, some decrease in fluorescent brightness will result, especially if the contrasting colors are widely separated spectrally.

Paints tinted to have approximately equal color under daylight and black light were prepared according to the recommendations given in the last column of Table I and measured for relative reflectance and emission with a Beckman spectrophotometer. Comparative reflectance and emission curves are shown in Fig. 1. The reflectance measurements were made with the monochromator ahead of the sample and the emission measurements with the reverse order. The relative sensitivity of the spectrophotometer system at different wave-lengths was determined by the use of a standard tungsten lamp of known spectral emission. The measurements on the fluorescent panels were then corrected for these variations in spectral sensitivity of the spectrophotometer. The difference between the spectral emission and reflectance curves for the reds, oranges, and yellows is the most interesting point in Fig. 1. As in most absorption colors, the difference between the spectral reflectance of red and yellow is shown by a shift of the selective portion of the curves to shorter wave-lengths and the yellow reflects all the wave-lengths that the red reflects. In contrast, the spectral emission curves of the yellow and orange fluorescent paints have characteristic maximum intensities. The chromaticity of the paints is shown in Fig. 2. The trichromatic coefficients were calculated from the spectrophotometric data in the usual way and the values for the coefficients $\bar{x}$ and $\bar{y}$ were plotted. The outside line in Fig. 2 represents the locus of pure spectrum colors and the star in the center represents complete non-selectivity, or white. The experimental emission data are shown in two solid curves connecting the five points which represent the colors of the five fluorescent pigments. One curve represents untinted paints and the other the tinted paints mentioned previously. Tinting resulted in an increase in purity and a slight decrease in emission intensity.

The broken curves represent reflectance data under illumination by white light. One curve shows the chromaticity of the same tinted fluorescent paints, the

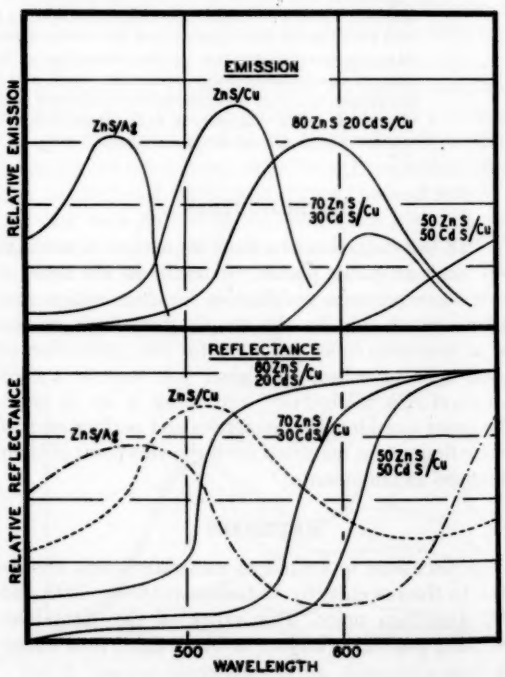

FIG. 1. Spectral emission and reflectance of tinted fluorescent pigments

other consists of values selected from published data[4] for artist's colors. It seems quite well established by these comparisons of emission and reflectance values (also tabulated in Table II) that fluorescent colors are more saturated than reflectance colors.

The fluorescent brightness of these high purity colors is, of course, dependent upon the intensity of the incident ultraviolet light. Our measurements showed that the fluorescent brightness was directly proportional to the near-ultraviolet light intensity when the latter was varied between 0.1 and 1000 microwatts per square centimeter. This range corresponds to a difference in brightness from 0.015 to 150 foot-lamberts for the copper activated ZnS and can be compared roughly with 0.1 foot-lambert for the brightness of fluorescent automobile instrument dials and 75 foot-lamberts for directional television screens. The relation between fluorescence and intensity of ultraviolet radiation is discussed later in connection with Table V. The fluorescent brightness attained in practice also is dependent upon the quantity of pigment present and the transparency of the binding medium in the near-ultraviolet. In other words, the concentration of pigment in the applied film and the film thickness will govern the fluorescent brightness if a certain minimum is not met. This is illustrated by Fig. 3 covering measurements on cellulose acetate sheeting of varying thickness containing a 75 ZnS-25 CdS/Cu pigment. Measurements over a black background show a sharp initial rise with an asymptotic approach to a maximum value similar to the curves obtained in measuring the hiding power of paints made with non-fluorescent pigments.

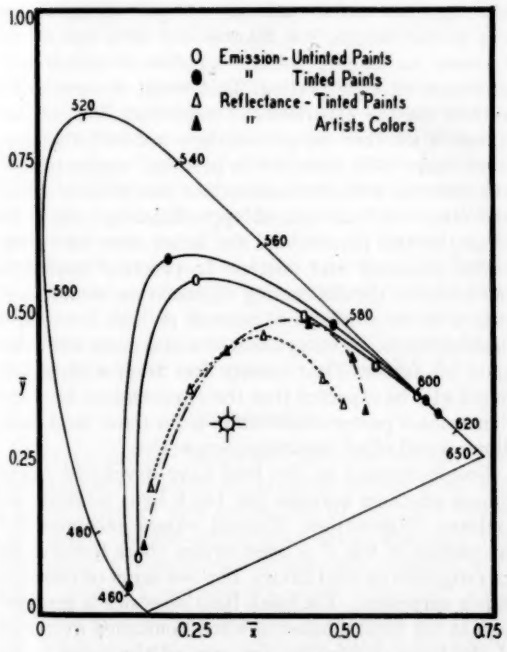

FIG. 2. Chromaticity diagram of fluorescent and absorption colors.

[4] Norman F. Barnes, J. Opt. Soc. Am. 29, 208 (1939).

TABLE II. Spectral emission and reflectance of fluorescent and absorption colors.

		Purity	Dominant wave-length	Trichromatic coefficients $\bar{x}$	$\bar{y}$
2205 Untinted	Emission	82	463	0.170	0.085
2205 Tinted	Emission	96	464	0.144	0.049
2205 Tinted	Reflectance	57	479	0.187	0.206
French ultra-marine*	Reflectance	75	468	0.175	0.115
2210 Untinted	Emission	53	536	0.252	0.560
2210 Tinted	Emission	55	528	0.215	0.591
2210 Tinted	Reflectance	18	501	0.254	0.372
Chrome green medium*	Reflectance	35	552	0.313	0.441
2215 Untinted	Emission	86	573	0.447	0.501
2215 Tinted	Emission	92	579	0.489	0.480
2215 Tinted	Reflectance	58	566	0.372	0.470
Cadmium yellow light*	Reflectance	82	575	0.450	0.482
2220 Untinted	Emission	94	590	0.561	0.419
2220 Tinted	Emission	100	603	0.641	0.359
2220 Tinted	Reflectance	63	588	0.471	0.392
Cadmium orange medium*	Reflectance	87	587	0.524	0.426
2225 Untinted	Emission	100	601	0.634	0.366
2225 Tinted	Emission	100	609	0.662	0.337
2225 Tinted	Reflectance	61	600	0.505	0.350
Cadmium red*	Reflectance	67	605	0.537	0.340
2200 Untinted	Emission	34	488	0.223	0.293
2100 Untinted	Emission	15	505	0.266	0.365

* From reference 4.

FLUORESCENT DISPLAYS

While color and brightness under specified conditions can be measured as physical characteristics, the evaluation of the effectiveness of applied forms involves the mental response of individual observers. One of the factors determining the effectiveness of a fluorescent display will be the masking effect of stray light. This might be expected to vary from 0.01 footcandle or less up to several footcandles but it should be possible to determine the relation between the ambient illumination and the fluorescent brightness required to produce an appealing display. In order to obtain some data on the question, a display was set up so that both the ambient illumination and fluorescent intensity could be varied. Forty-two observers were asked to give their rating of the display under the different conditions. About an equal number of men and women were used as observers. None had more than an average individual's knowledge or interest in the subject of luminescence.

The ambient illumination of the room was by indirect incandescent light. The fixtures were completely

TABLE III. Effect of ambient light on apparent fluorescence.

	Ambient illumination (footcandles) 0.002	0.02	0.12	1.3	10.5
Test I:					
Fluorescence 0.02 footcandles					
"Plainly seen"	80	20	10	—	—
"Just visible"	20	80	60	5	2
"No longer stands out"	—	—	30	95	98
Test II:					
Fluorescence 0.30 footcandles					
"Plainly seen"	100	100	85	2	—
"Just visible"	—	—	15	88	10
"No longer stands out"	—	—	—	10	90
Test III:					
Fluorescence 1 foot-lambert					
"Plainly seen"	100	98	98	78	45
"Just visible"	—	2	2	20	35
"No longer stands out"	—	—	—	2	20

screened from the observers to provide diffuse illumination of the entire room. This could be varied to give 0.002, 0.02, 0.12, 1.2, or 10 footcandles. Three levels of ultraviolet light intensity were provided. The first was by a 250-watt AH-5 lamp in a standard unit with reflector and roundel, UV-transmitting filter. The second was a 100-watt EH-4 flood lamp with a similar filter. The intensity of this lamp was reduced to 40 percent of full intensity by placing a fine metal screen over the lamp. The lamps have quite different beam patterns so the energy ratio was not exactly the same over the area of the display. The luminescent objects making up the display were arranged with those of weakest fluorescence closest and the strongest ones at the greatest distance from the light sources. This tended to equalize the brightness of the various items and make it possible to assign an approximate average brightness to the display as a whole for each of the exciting light sources. One of the test items was a painting done in fluorescent colors and provided with a 15-watt 360-BL fluorescent lamp filtered to cut out the visible and transmit the UV output of the lamp. This was mounted on the frame of the painting. The painting illuminated in this way attained a considerably higher brightness than the other items of the display and for this reason was evaluated separately as the third test. Table III shows the different levels of ambient illumination in footcandles, the fluorescent brightness in foot-lamberts and the observers' ratings. These are expressed as the percentage of the total of observers (42) who called the fluorescence of the exhibit material clear, barely visible, or not distinguishable.

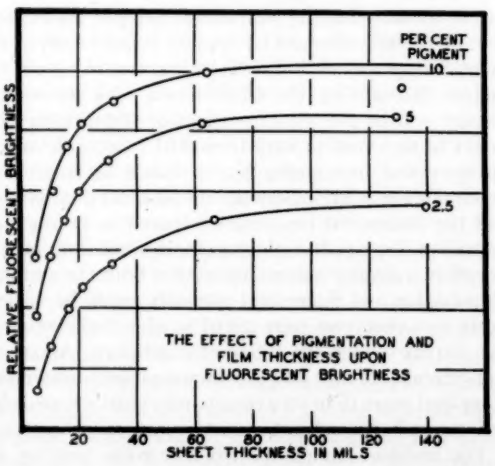

FIG. 3.

There is remarkable consistency in the observers' ratings. If one takes the maximum ambient illumination at which the fluorescence of the target is still "plainly seen" as an endpoint, the fluorescent brightness can be plotted against the ambient illumination. This gives the relation shown in Fig. 4. The equation for the relationship is found to be

$$\log F = 0.6 \log A,$$

where F is the minimum fluorescence brightness in foot-lamberts that will be plainly visible when A is the diffuse ambient illumination in footcandles.

This relationship was quite surprising. It had been expected that as the ambient illumination increased, the fluorescence intensity would need to increase at a much greater rate to maintain an equal rating. According to the results, the fluorescence does not need to increase so rapidly as the ambient illumination to maintain an equal rating. This result is undoubtedly correct for the experimental conditions, but one may question whether these conditions satisfactorily reproduce those to be expected in practical applications. In the test, the ambient illumination was entirely diffuse; the observers were seated approximately twenty feet from the test panels; and the latter were two-dimensional paintings and posters. In practical application out-of-doors the distracting illumination would be expected to be small point sources of high intensity or flashing lights. In many cases, the observers would be a good bit further than twenty feet from a display. It might also be expected that the requirements for a two-dimensional poster would differ from those for a three-dimensional effect requiring perspective.

People working in this field have developed rule-of-thumb relations between the black light intensity and ambient illumination. Typical values recommended[8] are plotted in Fig. 5 as open circles, those found in this investigation as solid circles. The two series of values are in fair agreement. The black light intensity is expressed here as the total number of watts consumed by the arc of the lamp divided by the area of the beam at the display.

[8] Switzer Brothers, Cleveland, Ohio, *Here's How for Best Results from Fluorescence*, Form 2029.

One reaction, independently voiced by a number of the observers, was that in Test III, a small amount of visible light seemed to improve the effectiveness of the display. It was not clear whether this was due to a better definition of the subject matter or to a reduction in the sharpness and depth of shadows.

In addition to the preceding data it was thought desirable to compare the attractiveness of fluorescent and normally illuminated displays. As the first step, a poster was prepared which appeared quite similar under black light and incandescent illumination. This in itself was difficult to make because the nature of fluorescent colors does not permit their reproduction by the normal pigments which depend upon selective absorption for their color. Duplicate posters were painted on black paper using fluorescent paints tinted so as to approximately match in daylight and black light. These were placed at the rear of black boxes approximately 1×1×2 feet. At the open end of one box a black light (Westinghouse type *K* with Corning filter No. 5040) was set up and shielded to illuminate only the poster at the closed end of that box. The other box was set up to be illuminated interchangeably by either a 7½-watt or a 25-watt inside-frosted incandescent lamp. The boxes were placed next to each other in an interior room where the ambient illumination was 10 foot-candles. Twenty-seven observers unfamiliar with luminescent pigments were asked to designate their preference between the two displays. The results of this survey, as shown in Table IV, were overwhelmingly in favor of the fluorescent display.

Photometric measurements indicated that the intensity levels in the boxes illuminated by incandescent light were twice as high using the 7½-watt lamp and twelve times as high with the 25-watt lamp. In spite of this wide difference in intensity levels, the appearance of the black lighted fluorescent display was so striking that, under any condition, at least 70 percent of the observers preferred it. The intense colors of the fluorescent emission combined with the deepness of the black background in the fluorescent poster apparently produced extreme adaptation conditions in the observers on looking first at the one poster, then the other.[6]

TABLE IV. Comparison of attractiveness of fluorescent and absorption colors.

Observer stationed	Number of observers preferring display under: Black light	7½-watt incandescent	25-watt incandescent
5 feet from display	24	3	—
10 feet from display	24	3	—
5 feet from display	20	—	7
10 feet from display	19	—	8

Fluorescent color in posters	Brightness of poster in box (foot-lamberts) Black light	7½-watt incandescent	25-watt incandescent
Green	0.19	0.37	2.6
Yellow	0.20	0.72	4.9
Blue	0.03	0.21	1.7

EFFICIENCY

Near-ultraviolet radiation[7] for the excitation of fluorescence is commonly obtained either from high pressure mercury arcs or the 360-BL series of fluorescent lamps. Nickel-cobalt glass filters are used with both lamps to absorb visible light and transmit ultraviolet above approximately 3200 angstrom units. Forsythe, Adams, and Barnes[8] have given the characteristics of mercury arcs commonly used in the production of near ultraviolet for exciting fluorescence. When used as white light sources these lamps produce from 30 to 40 lumens per watt. From 11 to 12 percent of the total energy of the arc is represented by radiation within the visible spectrum and only 2.5 to 3.0 percent falls in the ultraviolet below 3800 angstrom units. This is the portion used in the excitation of fluorescence and obviously any system using less than 3 percent of the energy consumed in a lamp will be expensive. The practical recovery is still lower because the nickel-cobalt glasses used as filters may pass as little as 25 percent of the ultraviolet radiation.

The development of the 360-BL series of fluorescent lamps has provided another source of near ultraviolet for the excitation of fluorescence in materials responsive to that radiation. These lamps are constructed and operate in the same manner as the normal fluorescent lamps. However, they are coated with a phosphor which converts the 2537 angstrom unit radiation of the low pressure mercury arc into longer wave-length ultraviolet. The emission of this phosphor extends from 3200 to 4200 angstrom units with a peak at approximately

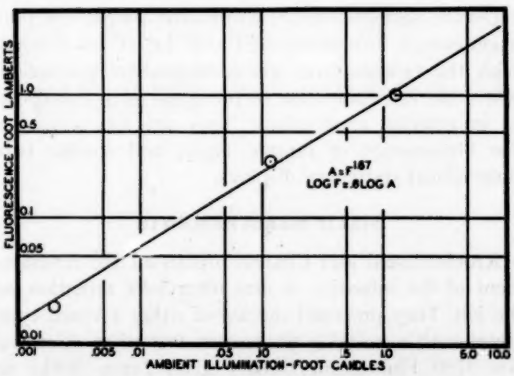

FIG. 4. Masking effect of ambient light on fluorescence.

[6] Harry Helson, J. Exper. Psychol. **23**, 439 (1938).
[7] E. W. Beggs, J. Opt. Soc. Am. **33**, 61 (1943).
[8] Forsythe, Adams, and Barnes, Journal Scientific Laboratories, Denison University **37**, 107 (1942).

3600 angstrom units. This emitted radiation in turn may be used to excite fluorescence in the wide variety of phosphors which respond to excitation by long wavelength ultraviolet.

The fluorescence of a number of commercial pigments excited by each of these types of lamps is shown in Table V. The first column for each lamp gives the slopes of the lines relating the ultraviolet radiation and fluorescence. These are close enough to 1.0 so that for most practical purposes the fluorescence can be taken as directly proportional to the ultraviolet intensity at the fluorescent panel. Normally neither the fluorescence nor the ultraviolet intensity will be found exactly proportional to the lamp wattage. In the case of the high pressure mercury arcs, more dense filters normally are used with 250-watt than with 100-watt lamps, and there is less control of the beam pattern of the stronger lamp. Like all fluorescent lamps the efficiency of the 360-BL type varies with its length or wattage and in this case also the density of filters is an added variable.

The second column in Table V under each type of lamp is an attempt to express the efficiency of the system as an illuminant. The values represent the fluorescence emission in foot-lamberts per watt consumed in the lamps, assuming the total radiation to be concentrated over an area of one square foot. They would correspond to the "lumens per watt" values used in the rating of light sources. For the reasons given in the preceding paragraph, it is only an approximation for the efficiency of either type of lamp with the various fluorescent panels. However, it serves to compare the two systems with each other as well as with other light sources. At best the fluorescent system gives low values even in comparison with the 10 to 20 lumens per watt from filament lamps. For the 30-watt, 360-BL fluorescent lamp the corresponding values are four to five times those obtained from the high pressure mercury arc and run up to 7.5 effective lumens per watt.

It is clear that where conditions permit their use the 360-BL lamps are a much more efficient source of ultraviolet than the high pressure mercury arcs for the excitation of fluorescence in these materials. The disadvantages are characteristic of fluorescent lamps; the radiation cannot be concentrated and the efficiency varies with the temperature. These limitations are serious where the radiation must be projected as in theatricals or in exterior applications. They are less serious in the illumination of murals, signs, and similar two-dimensional stationary displays.

FIELD MEASUREMENTS

Kraehenbuehl and Chanon[1] discussed the measurement of the intensity of near-ultraviolet radiation on the job. They proposed the use of either a visual type meter with a suitable fluorescent test piece (Corning No. 3750 Fluorescent Canary glass 2-mm thick) or an ordinary photovoltaic-cell light meter. The visual method has the range to cover all three of the measurements one needs: the ultraviolet intensity, the fluorescent brightness and the ambient brightness if it is high enough to be important. An objection to the fluorescent glass as a standard is that of all the materials examined in this study it was the only one to show a marked difference in response between the high pressure mercury arcs and 360-BL fluorescent lamps. When the glass was coated on the back and sides with a high reflectance flat white paint, a brightness of one foot-lambert was produced with near-ultraviolet radiation of 170 microwatts per square inch from a high pressure mercury arc or 125 microwatts per square inch from a 360-BL fluorescent lamp. Kraehenbuehl and Chanon reported that with a black background the fluorescent intensity of their sample of this glass was 0.49 foot-lambert for an ultraviolet irradiation of 400 microwatts per square inch. A recently purchased No. 3750 glass produced 0.55 foot-lambert under the same test conditions in our laboratory.

With a sufficiently sensitive galvanometer the three measurements can also be made with a photovoltaic cell; however, as shown below, the intensities are likely to be low for an ordinary light meter. Kraehenbuehl and Chanon[1] found that 27 microwatts per square inch of near-ultraviolet produced a reading of 1 footcandle in a General Electric Light Meter. The discrepancy is evidence of the necessity for calibration of individual light meters to be used in the measurement of near-

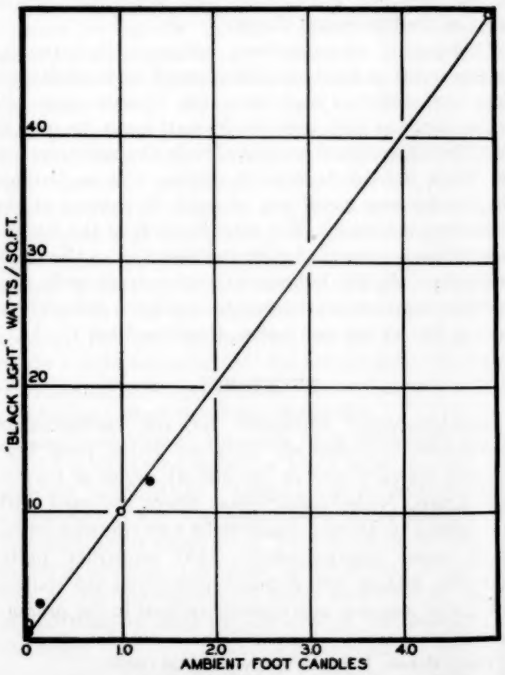

FIG. 5. Effect of visible light on amount of black light needed to produce noticeable fluorescence.

Instrument	Intensity of near-ultraviolet to produce a reading of 1 footcandle microwatts per square inch
General Electric light meter	60
Weston light meter	46
Photovolt No. 781 cell	42

ultraviolet radiation. In the current work, measurements of near-ultraviolet radiation were made over a period of several months with thermopile, photovoltaic cell, and visual light meter with fluorescent target. Once calibrated, the second gave the best reproducibility, and, of course, was the most rapid and simplest of the three.

APPLICATIONS

Some discussion of applications is warranted for, in order to be of practical value, fluorescent pigments must be incorporated into a supporting medium. Paints, lacquers, and enamels[9] can be prepared with these pigments using regular techniques although prolonged grinding is to be avoided. High fluorescence is most efficiently achieved by painting over a white-primed surface. One coat generally suffices since it is the surface layer of pigment which emits light. When used indoors, these colors should persist indefinitely since they are far more permanent than the fluorescent organic dyes which are used for textiles. The possibilities of fluorescent paints for decoration have been discussed recently in several journals.[10–12]

Plastics[13] offer another means for utilizing fluorescent pigments. Their transparency and lack of color permit good transmission of the exciting and emitted radiations necessary for high illuminating value. The use of both flexible and rigid types of plastic enables a widely diversified line of commercial articles to be fabricated which have the added utilitarian or decorative factor of luminescence. Molding granules and sheetings which contain luminescent pigments are now commercially available.

Although fluorescent porcelain enamel signs have been made only in a limited number of colors to date, their possibilities are not being overlooked. In a recent article, Duncan[14] says "While luminous porcelain enamel is at present a distinct novelty, its future is assured since it can be made to compare favorably with a Neon sign by the use of the proper amount of black light. The glow given off by the luminous porcelain enamel is a great deal different from anything that has been introduced in the advertising field."

Fluorescent paper[15,16] has been made both by incorporating pigment into the sheet and by applying a coating containing the pigment. The latter, being more economical, has been used in making wallpaper for use with black light for decorative effects. Billboard poster-stock coated with fluorescent pigments and printed with contrasting fluorescent inks makes very effective display advertising. There are many possibilities for fluorescent signs in advertising.[17] One scheme permits a change in copy under black and white light illuminations. In another, the featured portion alone can be seen under black light and the message can be read under the intermittently superimposed white light. Probably the greatest advantage is the three-dimensional quality which results in displays made up of fluorescent materials.

TABLE V. Efficiency of exciting light sources.

Sample	High pressure mercury arc[a] Slope of line relating fluorescence and ultraviolet energy	High pressure mercury arc[a] Foot-lamberts per watt per square foot[c]	360-BL fluorescent[b] Slope of line relating fluorescence and ultraviolet energy	360-BL fluorescent[b] Foot-lamberts per watt per square foot[d]
2200	0.98	0.35–1.1	0.99	5.3
2205	0.99	0.13–0.4	1.03	2.1
2210	1.06	0.4 –1.2	0.97	7.5
2215	0.96	0.45–1.3	0.98	6.0
2220	1.0	0.17–0.55	0.98	2.4
2225	1.1	0.02–0.08	1.05	0.4
2100	0.93	0.33–1.0	1.0	3.7

[a] 100-watt EH-4 and 250-watt AH-5 lamp with roundel, UV filters.
[b] 30-watt 360-BL and tubular (Corning 5874), UV filter.
[c] Based on total arc watts for 100-watt EH-4 lamp. The double values represent the difference due to the range in density of the roundel filters supplied for the lamps. The ultraviolet energies for the low and high values are 25 and 80 microwatts per square inch. Values for the 250-watt AH-5 with roundel glass filter are about 75 percent of the higher values for the 100-watt lamp.
[d] Since the efficiency of a fluorescent lamp varies with its length, these values will be different for lamps of different wattage or construction.

[9] L. H. Trott, Paint, Oil, and Chemical Review **107**, 9 (February 24, 1944).
[10] R. J. Elliott, J. Soc. Mot. Pic. Eng. **50**, 601 (1948).
[11] Architectural Record **100**, 115 (September, 1946).
[12] Architectural Forum **88**, 125 (June, 1948).
[13] V. A. Belcher, Modern Plastics **21**, 105 (February, 1944).
[14] R. F. Duncan, Enamelist **24**, 34 (March 1947).
[15] Paul A. Smith, Paper Trade Journal **118**, 123 (April, 13 1944).
[16] Myrtle Fahsbender, Illum. Eng. **94**, 159 (1949).
[17] M. A. Heikkila, Signs of the Times **120**, 30 (October, 1948); **120**, 44 (November, 1948).

Sodium and Lithium as Activators of Fluorescence in Zinc Sulfide

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Lithium and sodium dissolved in zinc sulfide act either as activators of fluorescence, or as quenchers, according to whether chlorine is present or not. The fluorescence occurs only at low temperatures and is excited by short-wave ultraviolet. The lithium band has a maximum at 4380A in the sphalerite modification of ZnS; the sodium band has a maximum at 3940A in sphalerite and at 3800A in the wurtzite modification.

The difference in the position of the bands for wurtzite and sphalerite and a shift found upon incorporation of CdS proves that we are dealing with electron-transfer bands. The centers of fluorescence are supposed to consist of lithium or sodium and chlorine ions occupying normal lattice sites. The levels involved in the fluorescence transitions are levels due to lattice ions, changed by the presence of the monovalent ions (indirect activation).

The quencher centers are supposed to consist of Li_2S and Na_2S incorporated in ZnS in such a way that the alkaline ions occupy two cation sites, while of two anion sites one is occupied by a monovalent sulfur ion and the other by an electron.

INTRODUCTION

ZINC sulfide luminophors are usually made by heating zinc sulfide with a small amount of silver, copper, or gold and 1–30 percent of a halide. The former elements are essential for a particular fluorescence and are called activators. The halides have long been supposed to act merely as a crystallizing agent and are usually called fluxes. Recently it has been recognized, however, that the anions Cl, Br, and I of the flux play an essential part in the formation of fluorescence centers.[1–3] The cations (Na, K, Li, Ca, Sr, Ba, Mg) are only of secondary importance, although according to Rothschild,[1] these ions may cause small differences in the fluorescence of copper-activated zinc sulfide.

In this paper it will be shown that Na and Li may enter the ZnS lattice and then either act as killers of a fluorescence due to other centers, or give rise to a fluorescence of their own. Ca, Sr, and Mg probably also enter the lattice, but these have no particular effects.

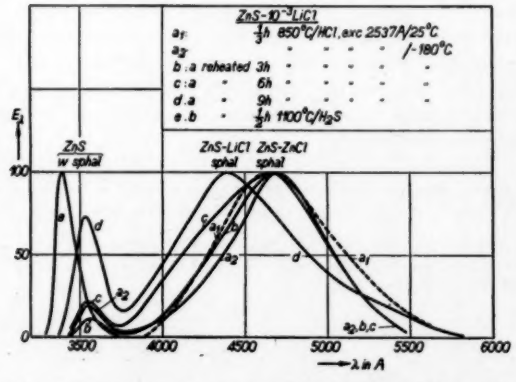

FIG. 1. Fluorescence bands observed with zinc sulfide containing lithium as an activator upon excitation by λ=2537A at room temperature and liquid-air temperature.

EXPERIMENTAL

ZnS–LiCl

ZnS heated with 10^{-3} LiCl at 850°C in a current of HCl gives a product of the sphalerite structure, showing a blue fluorescence upon excitation by ultraviolet radiation. At room temperature the fluorescence band has a maximum at 4600A; obviously it is the band of ZnS–ZnCl.[3] At −180°C we find a band with a maximum near 4730A and an inflection near 4400A, while an additional maximum appears at 3550A. The latter is also found in pure zinc sulfide: it is the fundamental fluorescence of ZnS, situated at the absorption edge.[4] The inflection indicates a new emission band caused by lithium.

In order to obtain this band separately it is necessary to find a method of preparation in which the blue ZnCl band is suppressed. For silver-activated zinc sulfides it has been found that the formation of ZnCl centers can be prevented by preparation in an atmosphere of H_2S–HCl with a low HCl content.[3] Application of this method to the present case remains, however, without success: if the preparation is carried out at 900°C the products do not fluoresce because of a lack of crystallization; if the preparation is carried out at a higher temperature (1200°C), the sulfide recrystallizes satisfactorily but still shows no fluorescence. The lack of fluorescence is not due to evaporation of the lithium because, although part of it certainly evaporates, a considerable fraction of the lithium added still can be detected in the final product. Moreover, the products are colored slightly reddish, which is not the case when lithium is not present.

Better results are obtained if a product made at 850°C in HCl is reheated for several hours at the same

[1] S. Rothschild, Trans. Faraday Soc. **42**, 635 (1946).
[2] J. W. Strange, Proc. Phys. Soc. **55**, 364 (1943).
[3] F. A. Kröger and J. E. Hellingman, J. Electrochem. Soc. **93**, 156 (1948).
[4] F. A. Kröger, Physica **7**, 1 (1940).

temperature in a current of hydrogen. Then the sulfide gradually loses its chlorine content; the fluorescence first changes from white blue to deep blue and is then totally quenched. Figure 1 shows the variation in the spectral distribution of the fluorescence: the peak at 4600A is replaced by one at 4380A. The fundamental fluorescence at 3550A remains practically unchanged.

Attempts to find the position of the lithium band for the wurtzite modification of ZnS failed. Heating at a temperature above 1050°C as required for the transition caused the blue fluorescence to disappear while the product became slightly reddish, just as was found with the products directly heated at such a high temperature. The fundamental fluorescence of ZnS remains with a peak now at 3400A showing the usual difference of 150A with the sphalerite modification.

After preparation of the luminophor at a high temperature, lithium not only does not act as a center of fluorescence but even acts as a quencher for the fluorescence due to other centers. If for instance, ZnS containing 10^{-3} LiCl is heated for half an hour in HCl at 900°, and then for half an hour in H_2 at 1200°C, the product is not fluorescent, while a zinc sulfide without lithium subjected to the same treatment still shows a reasonably strong blue ZnCl fluorescence.

ZnS—NaCl

ZnS heated with 5.10^{-3} NaCl at 900° in an atmosphere of HCl shows the normal ZnS—ZnCl fluorescence with a maximum at 4600A, both at room temperature and at liquid air temperature. When such a product is reheated at the same temperature in a current of hydrogen, the fluorescence characteristics rapidly change: within 30 minutes the blue fluorescence disappears and is replaced by a low temperature fluorescence with a maximum at 3920A (Fig. 2).

After prolonged heating this band in turn disappears. These variations are accompanied by a loss of chlorine: even if we start with a very high sodium-chloride content (10 percent NaCl), less than 10^{-4} chlorine is left after heating in hydrogen for one hour. Apparently the 3920A band appears at a reduced chloride content, while it disappears again when all the chlorine is gone.

If the product with the 3920A band is reheated at 1050°C and then cooled, the zinc sulfide is transformed from the sphalerite into the wurtzite modification and the position of the fluorescence band changes to 3800A (Fig. 2).*,[5] A product showing this band can also be obtained by heating ZnS with 5.10^{-3} NaCl for half an hour at 1200°C in H_2S. Then the fluorescence in the 3800A band is weaker and the fundamental fluorescence of ZnS is correspondingly stronger. This effect is due to evaporation of NaCl. If the heating is carried out in hydrogen the fluorescence is weaker still, for the same reason.

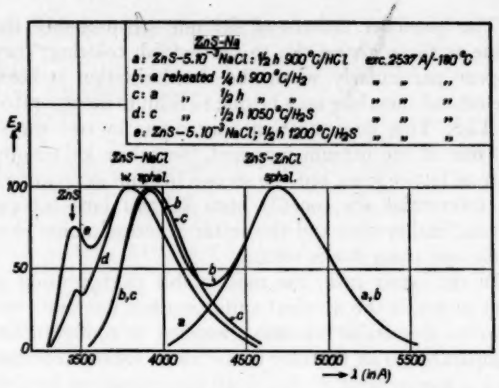

FIG. 2. Fluorescence bands observed with zinc sulfide and zinc cadmium sulfide containing sodium as an activator upon excitation by λ=2537A at liquid-air temperature.

Spectrographic analysis shows that products with a strong sodium band contain about 10^{-4} gram atoms Na/mole ZnS.

ZnS—K, Ca, Sr, Ba, and Mg

ZnS heated with 10^{-3} KCl, $CaCl_2$, $SrCl_2$, $BaCl_2$, or $MgCl_2$ at 900°C in HCl show the blue ZnCl fluorescence. Reheating for several hours in hydrogen removes most of the chlorine. Apart from a few exceptions, the products then only show the ultraviolet fundamental fluorescence of zinc sulfide at liquid air temperature.

In some cases with calcium, a band at 3800A was found, which proved to be due to a trace of sodium present in the calcium salt.

ZnS—CdS—Na, Li

When experiments as described above are carried out with (Zn—Cd)S instead of ZnS the results are essentially the same, the only difference being that the emission bands are displaced toward the long wavelength side (Fig. 2). This, together with the differences found between wurtzite and sphalerite, proved that we are dealing with electron transfer bands, just as is the case in ZnS—AgCl, ZnS—CuCl, etc.

DISCUSSION

As was shown in the experimental part, incorporation of lithium and sodium in zinc sulfide may give rise to fluorescence centers or to quencher centers. Fluorescence centers are only formed when halide is present. In analogy to what has been proposed, for the fluorescence centers of copper, silver, and zinc,[3] it seems reasonable to assume that the fluorescence centers consist of NaCl and LiCl incorporated in zinc sulfide in such a way that Na and Li occupy zinc sites and the chlorine sulfur sites.

* This band is obviously identical with the one we mentioned in a previous publication as "a new band of unknown origin." (See reference 5.)

[5] See reference 5, p. 177.

The quencher centers of lithium are probably the same as those giving rise to the reddish coloring; they appear particularly when the dechlorination is completed and therefore may be due to lithium incorporated as Li_2S. This incorporation may occur in two ways: (1) one of the lithium ions and the sulfur ion occupy normal lattice sites, but the second lithium ion occupies an interstitial site, or (2) both lithium ions occupy normal cation sites and the sulfur a normal anion site, while one anion site is vacant.

In the latter case, the most stable configuration is that in which the divalent sulfur ion has lost one electron to the anion vacancy, forming a configuration comparable to an F center in the alkali halides together with a monovalent S^- ion. Both configurations involve a large increase in energy but are favored by entropy and may therefore occur at high temperatures, as is actually observed. A similar explanation has been put forward for quenching centers formed by copper,[6] and the drop in efficiency in ZnS—AgCl at concentrations greater than 10^{-4} gram atoms Ag/mole[3] must probably be explained in the same way.

The fact that the killer activity of sodium is much less pronounced than that of lithium may be due to a smaller solubility of Na_2S.

The lack of fluorescence with potassium is probably due to its large ionic radius which prevents its incorporation. The same explanation might hold for barium and strontium; calcium and magnesium, however, will certainly dissolve in zinc sulfide, be it only up to a small concentration. Yet they do not form fluorescence centers. Considering that fluorescence and killer activity have now been observed with Cu, Ag, Zn, Au, and Pb, while in all these cases these elements are assumed to be in the monovalent state, it seems reasonable to assume that these effects are essentially connected with the presence of monovalent ions.** Such a general effect of monovalent ions can be explained in two ways: in the first place it may be that the levels involved are not due to the foreign ions themselves but to lattice ions next to the foreign ions, changed by the missing charge. This explanation applies to the fluorescence (indirect activation[7]). It may also be, however, that the incorporation of monovalent ions in all cases causes a similar new configuration (secondary activation[7]). This applies to the incorporation of monovalent sulfides if this should take place with the formation of an anion vacancy (case (2) mentioned above). Inversely, the fact that incorporation of monovalent sulfides generally seems to cause the same effect, *viz.*, quencher activity, may be seen as an argument in favor of this way of incorporation. The quencher centers then would be either the anion vacancies containing an electron or the monovalent sulfur ions.

ACKNOWLEDGMENTS

The author wishes to acknowledge the help of Messrs. J. E. Hellingman and J. Dikhof who carried out the preparations, and of Mr. Th. P. J. Botden under whose supervision the spectral distributions of fluorescence were measured.

[6] F. A. Kröger, *Some Aspects of the Luminescence of Solids* (Elsevier Publishing Company, Inc., New York and Amsterdam 1948), p. 238.

** This statement is only valid for fluorescence of the transfer type; for characteristic fluorescence it does not hold, as is proved by the case of zinc sulfide activated by manganese.

[7] See reference 6, Chapter I, Section 6.

Phosphorescent Response to Sinusoidal Excitation

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(Received May 2, 1949)

A mathematical study of the variation of brightness with time, of a theoretically exponential decay phosphor excited by a sinusoidal current as a function of the relative decay time and frequency of excitation, shows a phase lag and a decrease of amplitude of response increasing with the relative increase of decay time. The response is never sinusoidal and the increase in brightness is never as great as the decrease, which is characteristic of systems of a constant decay rate k involving the factor $K/(K+k)$.

THIS is a mathematical study of the brightness variation of a phosphor, with exponential decay, produced by an excitation varying in intensity according to the sine function, as it depends on the relative rate of decay and the periodic time of the excitation.

Excitation is treated as due to a cathode-ray beam although the results presumably would apply as well to photo-excitation with a sinusoidal variation in intensity of illumination. Since the cathode-ray tube gives half-wave rectification, we assume a steady direct current modulated with a sine wave of such amplitude that at maximum negative value the total current is just zero. The voltage of the beam is assumed to be constant and sufficient to excite the whole depth of the phosphor.

Assuming that the phosphor contains n excitable centers and that the brightness is proportional to the number n^* of excited centers, we can write,

$$dn^*/dt = I(n-n^*) - kn^*, \quad (1)$$

where k is the decay exponent which is the reciprocal of τ the time to decay to $1/e$ of the initial brightness and I is the equivalent exciting intensity of constant value. However, if $I+I_0 \sin\omega t$ to give sinusoidal excitation, is substituted for constant I, the equation cannot be integrated. J. C. Kech has shown that if the number of unexcited centers, $n-n^*$, is used as the variable, integration can be found by series expansion from

$$dx/dt = -(I+I_0 \sin\omega t)(n-n^*) - k(n-n^*) + kn^*, \quad (2)$$

to

$$n-n^*/n = ke^{I_0/\omega \cos\omega t}(1/k+I) - (I_0\omega/(k+I)^2+\omega^2) \times[(k+I)\cos\omega t + \omega \sin\omega t] + \cdots. \quad (3)$$

Obtaining numerical values from this series is remarkably tedious except at $\omega t = 90°$ and 270° where it becomes rapid and accurate, affording two definite points on each curve. This series can also be used to show that the maxima and minima of these curves occur when $\sin\omega t$ equals $\cos\omega t \times (k+I)/\omega$ from which are obtained the following values for the case where $1/\tau = k = I = I_0$ and τ has indicated values:

τ	1/40 cycle	1/4 cycle	1/2 cycle	1 cycle	2.5 cycles
Maximum	94° 29′	128° 8′	147° 31′	162° 21′	172° 45′
Phase lag	4° 29′	38° 8′	57° 31′	72° 21′	82° 45′

In order to obtain closely spaced points on the curves with reasonable accuracy and speed, Eq. (1) is integrated to give

$$\Delta n^*/n = (I(n-n^*) - kn^*)(1-e^{-(I+k)\Delta t}), \quad (4a)$$
$$= [1-(k/k+I)-(n^*/n)](1-e^{-(I+k)\Delta t}), \quad (4b)$$

where Δn^* is the change in number of excited centers over the interval Δt. Dividing a cycle into 40 parts and assuming the excitation over each part to be I plus the average value of the sine times I_0 over the interval or $(\cos\omega t)/\omega$, then the increments Δn^* over each part of the cycle can be found which allows the course of the build up and decay to be followed throughout the cycle as shown in Fig. 1.

Here the brightness is plotted against a linear time scale together with the exciting current. The latter is merely a sine wave. The wave shape of the former is definitely non-sinusoidal and the phase lag increases as the phosphorescence increases in duration. These values are approximately those for the equilibrium state after the transient has passed.

Possibly the most conspicuous feature for the short phosphorescence is that the positive or bright part of the cycle does not rise proportionately to the excitation. The dark half of the cycle follows the excitation much more closely; as the phosphorescent time increases, the phase lag becomes more conspicuous and the brightness follows the excitation less and less until, for very long phosphorescence, the brightness is practically constant at the mean value due to the constant component of excitation.

In Fig. 2 the same results have been plotted so as to bring out some further peculiarities of the response. This is a drawing of the presentation on an oscilloscope screen if the horizontal deflection is made proportional to the exciting intensity and the vertical deflection is proportional to the resultant brightness. If the brightness corresponded in phase and magnitude to the excitation there would be a straight line at 45°. If it were simply out of phase there would be an ellipse of 45° major axis becoming a circle at 90° lag.

At $\tau = 1/40$ cycle there is a loop near the 45° line in the dark phase and again the noticeable lack of brightness response in the bright phase. Possibly something quite similar to this hysteresis-like loop could be obtained with magnetizable material, if the magnetizing

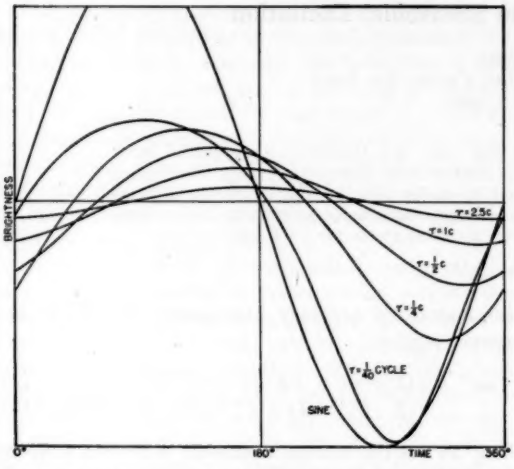

FIG. 1. The brightness of a phosphor with sine wave excitation plotted against time during a cycle.

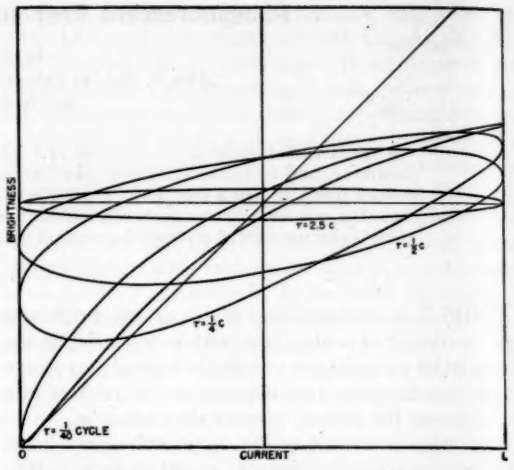

FIG. 2. The brightness of a phosphor with sine wave excitation plotted against the intensity of excitation.

field did not reverse but simply went to zero as in this case.

At $\tau=1/2$ the loop is nearly an ellipse but not at 45° and at $\tau=2.5$ cycles the circle is flattened nearly to a line by the cumulative effect of the long phosphorescence.

This study has been confined to the case where $k=I=I_0$. Investigation of other ratios may give quite different results. The effect of short-high intensity pulses in producing build-up may also be found, as well as the relative effect of rectangular pulses as compared with sinusoidal excitation.

The Asymptotic Behavior of Spontaneous and Forced Decay*,†

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(Received May 2, 1949)

The decay of phosphors under the influence of stimulating radiation can be investigated in a manner which avoids some of the complications impairing the significance of most decay measurements. The stimulated decay of an infra-red-sensitive strontium sulfide phosphor was measured. The complicating influence of spontaneous decay was practically eliminated. A phosphor with comparatively weak absorption of the stimulating and of the exciting radiation was selected and an extremely thin layer of the material was used, so that homogeneous excitation and stimulation were secured. The procedures of exhausting the phosphor and of measuring its stimulability were separated in principle and the stimulating intensity was kept constant throughout the exhaustion. The sensitivity to stimulation was measured over a range of six powers of ten, and the forced decay was carried to nearly complete exhaustion of the phosphor. This made it possible to determine the residual light-sum over a large range, and a region of very weak excitation of the phosphor was included. A further elimination of complicating factors is achieved by studying the infra-red-sensitivity as a function of the residual light-sum. The results of these measurements show strong evidence of second-order kinetics for the later stages of decay.

A suggestion that a certain kind of superposition of second-order processes should lead to an exponential asymptotic behavior of the decay is shown to be based on a fallacy.

IN our attempt to simplify the luminophors used for the investigation of phosphorescence (cf. the preceding paper "Simplified Lenard Phosphors"), we have also endeavored to gather physical data of basic significance. In this paper we report the results of such an attempt made with respect to some of the characteristic properties of infra-red-sensitive phosphors.

The interpretation of the phenomena of phosphorescence, particularly of decay curves and thermoluminescence, depends upon the answers to two much-discussed questions:

First—Is the decay simple, represented by one well defined decay constant, or is it the result of a superposition of components, with a spread of the decay constants over a relatively large range of values?

Second—Can trapped electrons, once they have been lifted out of their traps by thermal motion, be efficiently retrapped, be it by the trap from which they come, or by other traps? These questions are just as relevant for decay forced by radiation as they are for thermoluminescence and for spontaneous decay.

We have reported earlier measurements of the stimulated decay of Eu-Sm-activated strontium sulfide, which seemed to convey definite information on both points. For this purpose measurements of absorption in the stimulation band** were combined with measurements of stimulability. Both magnitudes increase during excitation and decrease during decay, but the relation between them is quite different in the course of these two processes. This relation is shown in Fig. 1. The absorption value at the peak of the stimulation band is undoubtedly a good measure of the number of excited states. The curves show that this number does not uniquely determine the stimulability. The decay branch (the lower curves of these hysteresis loops) indicates that those excited states that are most sensitive to infra-red radiation disappear first: The stimulability drops rapidly, while only a comparatively small number of excited states is removed, and in the later stages of this exhaustion by stimulation very insensitive states only remain. The build-up branch, quite plausibly, does not show such discrimination of states of different stability. Thus, as far as stimulated decay is concerned, these curves seem to prove a spread of the decay constants. Note that this conclusion is reached independently of any assumption concerning the order of the decay reaction.

The low stimulability in the later stages of decay means that electrons, after they have absorbed infra-red photons large enough to produce emission, very frequently do not emit, but are retrapped either by falling back, or by being captured by other empty traps. The arguments leading to this conclusion are discussed in Appendix I.

The importance of these problems made it desirable to obtain further experimental material free from some objections which could be raised against the former rather cursory measurements. *First*, we tried to eliminate the distorting effects which the strong absorption of stimulating and emitted light produces in a thick layer of the Eu-Sm phosphors. It is known that this effect is difficult to account for by mathematical analysis, particularly if scattering is involved, and the true absorption changes in the course of decay. We used, therefore, Ce-Sm-activated phosphors which have a very much weaker infra-red absorption and a negligible absorption of the emitted light; and we used them in extremely thin layers, consisting of grains of about 5μ in diameter thinly scattered on a back-silvered mirror.

Second, the somewhat problematic determination of absorption from diffuse reflection measurements was replaced by a determination of the residual optical light-sum, a much more appropriate measure of the number of effectively excited states (cf. also Appendix I). The required nearly complete exhaustion of the phosphor by

* Presented at the Winter meeting of the Optical Society of America, March 10–12, 1949, New York, New York.

† Communication No. 1259 from the Kodak Research Laboratories.

** Determined by measurements of diffuse reflection, as described in an earlier paper. See reference 5.

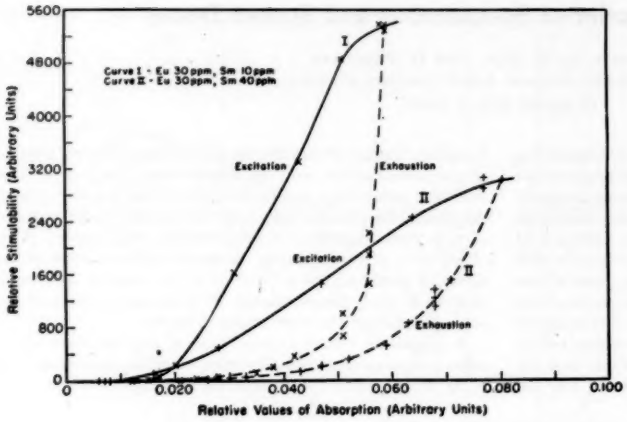

FIG. 1. Hysteresis curves of strontium sulfide phosphors activated by europium and samarium.

strong stimulating light is fairly easily achieved with Ce-Sm while it was nearly impossible with Eu-Sm-activation.

Third, the exhaustion measurements were extended to very low brightness levels, so as to cover a very large range of stimulabilities.

Fourth, we separated the operation of measurement of stimulability from that of exhaustion by stimulation. The latter was produced with very strong light of constant intensity (cf. Appendix II).

The arrangement used in these measurements is shown in Fig. 2; the filtered light from a 100W lamp, concentrated by a suitable optical system so as evenly to illuminate the phosphor, is used for exhaustion; the 7½W lamp is used for the measurement of stimulability. The photo-multiplier tube with its amplifier and range selectors was very carefully calibrated, the light sources were stabilized, etc. In order to avoid interference of spontaneous decay with the forced decay, we started the measurements 1½ hours after excitation, and most of the measurements were then obtained within a few minutes.

It would have been desirable to use monochromatic exhausting radiation, but sufficient intensities could not have been obtained with the equipment then at our disposal. We used filtered deep-red and infra-red light. The band mainly effective was the infra-red stimulation band at 1μ but a small contribution by the band at 600 mμ, reported earlier, was included.

Recent experiments in our laboratory indicate that the contribution by the shorter wave-length band may influence somewhat the exact shape of the exhaustion curve;†† we believe, however, that the main conclusions of this investigation are not affected by this distortion.

A set of exhaustion curves was measured after excitation with different intensities. Figure 3 shows such curves in a plot analogous to that of the former hysteresis curves. The abscissa shows the residual light-sum; the ordinate, the stimulability. The curves have the same general characteristics as the former set and the conclusions concerning the coexistence of states of different stimulability, and concerning retrapping, seem to be supported by these more reliable data. The fact that the curves show a less pronounced hysteresis effect than the data of Fig. 1 may well be due to the long waiting period after excitation which eliminates the most unstable states. The possibility that the hysteresis effect is still due to the finite thickness of the sample seems remote, but experiments to decide this point would be desirable. It is of interest to present our experimental data in more detail. Figure 4 shows the curves of forced decay in a log-log plot of stimulability *versus* time, extending over six powers of ten in stimulabilities. The general shape of the curves resembles that of a simple second-order decay. A closer inspection

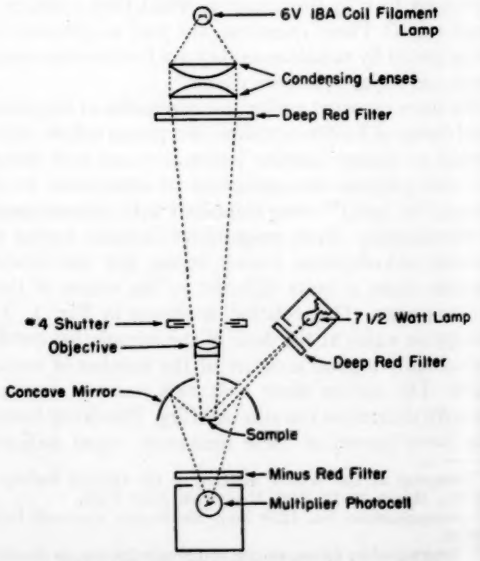

FIG. 2. Set-up for exhaustion measurements.

†† The band at 1μ is apparently more rapidly exhausted than the 0.6μ band, particularly if radiation around 1μ is used for the exhaustion.

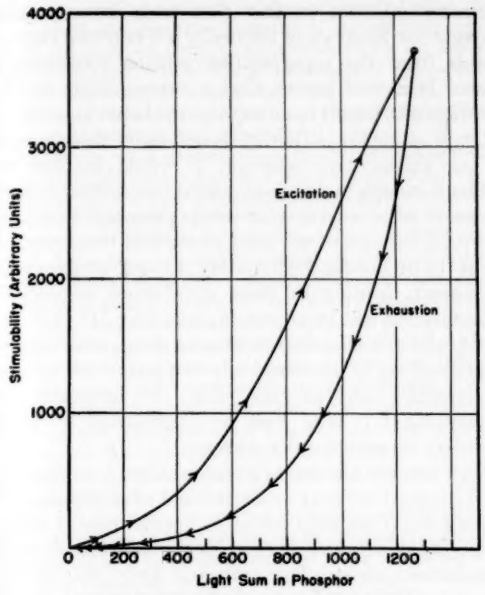

FIG. 3. Hysteresis curve for "STD. VII."

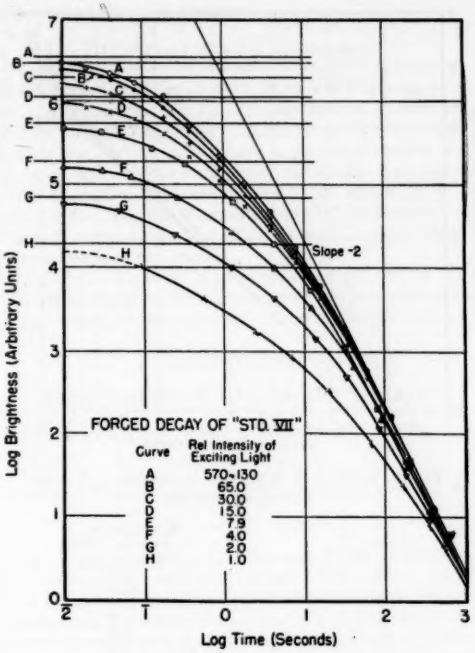

FIG. 4. Forced decay of "STD. VII."

shows strong deviations in the initial part of the curves. In the later stages of the decay, however, the curves approach each other very closely, and towards the end of the measurements, initial differences of a factor of one hundred are largely wiped out. This convergence towards the same decay curve is to be expected in second-order decay, and so is the common asymptote of a slope of -2. In the first few curves, in which the decay can be followed far down from the initial level, there seem to be fairly long straight-line portions with that slope. The straight line with slope -2 is expected in a simple bimolecular decay only after a considerable drop of brightness. The deviation from the $1/ct^2$ asymptote is expected to be still quite appreciable after a drop by a factor of 100. It is useful to consider, instead of the ordinary equation of second-order decay, the corresponding differential equation. The relation

$$B = \text{const} \times L^2,$$

where B denotes the intensity of emission and L the light-sum, should hold strictly for a simple second-order process throughout its course, even at the beginning. Thus, if, as Fig. 4 indicates, the strong deviations from a simple second-order process occur only at the beginning, we should expect a much longer straight-line portion in the graph of $\log B$ *versus* $\log L$ than we would in the graph of $\log B$ *versus* $\log t$. Furthermore, the decay of both light-sum and brightness may still be distorted by a variety of complications, such as residual absorption effects, time-lag effects, and the fact that the exhausting light was not monochromatic. Such distorting influences will affect both the light-sum and the stimulability in the same direction, if not to the same extent. The clearest results are therefore to be expected from an analysis of the relation between stimulability and light-sum. Figure 5 shows a plot of the logarithm of stimulability against the logarithm of the square of the light-sum. The lower left end of this plot corresponds to long-continued exhaustion. The curves converge very precisely towards a straight asymptote with a slope $=1$. The stimulability is, thus, proportional to the square of the residual light-sum over 3 or 4 powers of ten. This would be strongly suggestive of second-order decay.

It has often been discussed what decay law would result from a bimolecular recombination mechanism not complicated by superposition of different components. The various treatments of the problem agree in one point: The longer the decay proceeds, the more it will approach simple second-order kinetics. This may be regarded as an example of the general rule that the simplest relations between experimental data and the fundamental mechanisms in solids are to be expected at low levels of excitation where the crystals are in a condition nearest to their normal state. In the present case, this condition is realized by the fact that after long decay most of the traps are in their normal (empty) state. During the initial stages of excitation, similar, though not identical, simplified conditions exist. Earlier measurements have shown that in this case, too, the stimulability over a large range varies with the square of the light-sum. These older measurements, together with the data of Fig. 5, seem to demonstrate clearly the existence of bimolecular decay, and the validity of

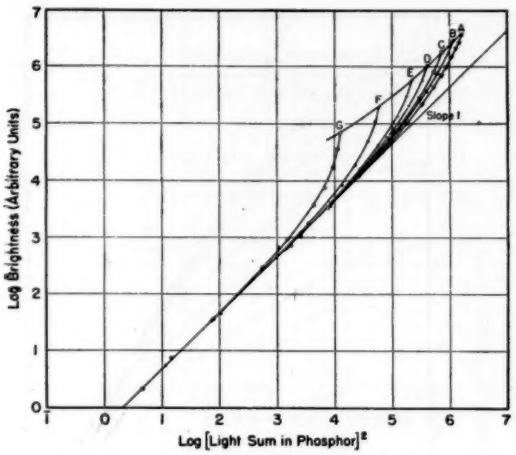

FIG. 5. Relation of brightness to residual light-sum during exhaustion.

Curve	Rel. Intensity of Exciting Light
A	570 and 130
B	65.0
C	30.0
D	15.0
E	7.9
F	4.0
G	2.0

second-order kinetics over a large range, extending fairly near to full excitation.‡

We are aware, of course, that the "asymptotic" behavior shown in Fig. 4 can also be represented by a superposition of exponentials. (Cf. Appendix III.) If this interpretation is maintained, however, it would be necessary to explain specifically why a distribution of decay constants prevails which "simulates" so closely a second-order decay.

On the other hand, there arises an apparent difficulty for the second-order interpretation. The hysteresis curves seem to show that traps with various decay constants contribute to the decay, and the question arises whether a superposition of second-order decays, must, or even can, yield a $1/t^2$ decay.

At least for one kind of superposition, a serious doubt has been raised in this respect. A peculiar scheme of superposition of bimolecular processes with different constants has been suggested by Antonov-Romanovski,[1] and a discussion of this case has led Ellickson and Parker[2] to conclude that "at large values of the time, the brightness *versus* time curve should be a straight line on semi-log paper. This is quite a remarkable result since it indicates that the interaction of a number of second-order processes can give, at large values of the time, an exponential decay such as is associated with a first-order process." The reasoning given by these authors indicates in fact that such an exponential asymptotic behavior of the decay not only can but must result from the superposition scheme considered by them. It is well known that a superposition of exponentials may result in an asymptotic behavior with $1/t^2$. If, now, a superposition of second-order decays results in an exponential behavior, it would become very difficult indeed to draw any useful conclusions from the shape of decay curves. Our results presented here would prove, if they prove anything at all, that the decay must be of the first order. Fortunately, a closer scrutiny of the arguments leading to these conclusions resolves the difficulty. It will be shown in Appendix III that for a large class of initial distributions of decay constants, the superposition in question leads to a power-law decay as asymptotic behavior and that, in particular, the asymptote $1/t^2$ may well be approached by superpositions of second-order decays.

The result of the investigation is, thus, a confirmation of the spread of decay constants and of retrapping. The experimental material indicates, furthermore, a second-order decay scheme, at least in the late phases of the exhaustion process. This makes it likely that at least part of the retrapping is of the bimolecular kind and that it is to some extent caused by traps of a depth comparable with that of the traps from which the electrons are lifted by stimulation.

APPENDIX I

Significance of the Spread of Decay Constants

In the case of spontaneous decay or thermoluminescence, the significance of the decay constants and the existence of a spread of their values over relatively large ranges has been discussed frequently. In Lenard's center theory, the size of the centers was regarded as responsible for these differences. Later, the concept of an electron trap was introduced into a strictly monomolecular model of the luminescence mechanism[3] and the decay constant was written as:

$$\alpha = s\epsilon^{-E/kT}.$$

In this model, variations of the absolute rate constants, s, or of the activation energy, E, or of both, were considered as possible causes of variations of α. It was pointed out that the two factors may be separated by an investigation of the temperature dependence of decay. More recently, most authors, following Randall's[4] example, have considered variations of trap depths only. In order to account for a given variation of α, a much larger variation of s is required than of E. Such large s-variations, however, may very well occur and play an important part, at least in some cases.

In the case of stimulated decay, the decay constant will be of the form of a product, βJ, of the stimulating intensity, J, and a factor, β, which may be described as a sensitivity constant. This constant depends, in turn, upon several factors, one of which is the absorbing cross section of the filled traps for the light used in the stimulation experiment. With an absorption band of constant shape, this factor is not likely to vary as the exhaustion proceeds. The constancy of the absorption band is strongly suggested by experiments published elsewhere.[5]

‡ This may indicate that at "full excitation" a large majority of traps still remain unfilled.

[1] V. V. Antonov-Romanovski, J. Phys. Acad. Sci. U.S.S.R. **2**, 157 (1942).

[2] R. T. Ellickson and W. T. Parker, Phys. Rev. **70**, 290 (1946).

[3] F. Urbach, Wien. Ber. (IIA) **139**, 363 (1930).

[4] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. **A187**, 366 (1945).

[5] F. Urbach, H. Hemmendinger, and D. Pearlman in *Preparation and Characteristics of Solid Luminescence Materials* (John Wiley & Sons, Inc., New York, 1948), Chap. 16.

Another possibility, however, requires attention. Assume that the comparatively insensitive condition of the phosphor represented by the lower part of the exhaustion branches in Fig. 3 would be due to the occurrence of a large percentage of non-radiative processes in the return of the excited electrons to the ground states. The various excited states would represent phosphorescence components of different "storage efficiency." In that case, the ratio between the absorption coefficient and the total residual light-sum would gradually increase in the course of the absorption process. If stimulability were plotted *vs.* light-sum and *vs.* absorption, curves of totally different shapes would be obtained. Measurements carried out by Dr. H. Hemmendinger have shown that this is not the case. Thus, the percentage of trapped electrons which, upon continued stimulation, produce an emitted photon seems to remain approximately constant throughout the course of exhaustion.

The fact remains, however, that in the lower part of the exhaustion curve, a great many electrons absorb infra-red photons without subsequent emission of a photon of the normal emission band. Thus, each of these electrons absorbs, on the average, several photons of stimulating light before one of these absorption acts brings it back to the ground state. This seems to prove that these electrons, after having been lifted out of their traps, are recaptured in the same trap or in another one, so that they are again capable of absorbing infra-red photons.[a]

While this argument represents a conclusive proof of effective retrapping, at least in the later phases of absorption, it does not necessarily imply bimolecular retrapping. If the retrapping is by the original trap only, the kinetics of decay may be of the first order.

APPENDIX II

The Exhaustion Measurements

Our older measurements of exhaustion curves were carried out by measuring the stimulated brightness produced at the start with a constant weak stimulating intensity. As the stimulated brightness became inconveniently low, the stimulating intensity was increased so as to maintain reasonable brightness levels. The decay was assumed to be accelerated in proportion to this increased intensity. The stimulation was stepped up in this manner two or three times in the course of one experiment and the various parts were combined into one curve by carrying out the simple reduction just indicated. Much the same procedure was adopted also by Ellickson and Parker.[3] We do not feel, however, that a completely satisfactory justification for this procedure has been given. One possible check, the absence of bumps at the points of intensity change in the exhaustion curves obtained in this manner, is a fairly insensitive test, and in some curves indications of such bumps have actually been observed. Another justification could be sought in the fact that our extensive measurements of the relationship between stimulating intensity and stimulated brightness yielded a very good proportionality over a large range of intensities. However, the required "reciprocity law" follows from that proportionality only with some additional assumptions. As an example, consider the following general form of a possible differential equation of the stimulated decay:

$$-B=dL/dt=-\beta(t)If(L). \qquad (a)$$

In this equation, L represents the light-sum; I, the stimulating intensity; $f(L)$, a function of the light-sum; and $\beta(t)$, the stimulability, which is assumed here to be explicitly dependent upon the time. By integrating, one obtains:

$$\int dL/f(L)=F(L)=I\int\beta(t)dt+\text{const.} \qquad (b)$$

L will be a function of the product, It, only if $\beta(t)$ happens to be constant. Although this is a plausible assumption, at least for the elementary components of any complex decay, it is by no means necessarily true for the total decay. It may well happen, for example, that a spontaneous stabilization of the excited states occurs while the exhaustion is proceeding. We do not suggest that this is actually the case, but this example shows that the proportionality of B and I expressed by Eq. (a) may well be valid while the reciprocity law may not hold.

In view of this situation, it was considered safer to use for our new exhaustion measurements a procedure which would not make use of the reciprocity law, although it does use the proportionality.

APPENDIX III

Superposition of Bimolecular Decays

The simple elementary equation of bimolecular decay,

$$dn/dt=-\alpha n^2, \qquad (1)$$

has sometimes been applied to components of a complex decay,

$$dn_i/dt=-\alpha_i n_i^2, \quad \Sigma\, n_i=N \qquad (2)$$

where n_i denotes the number of electrons of the ith kind; α_i the decay constants characteristic for that kind and N the total number of excited electrons. A superposition of such components can be expected if the recombination of the n_i electrons of the ith kind can occur only with the n_i holes left by electrons of that kind. This would be valid, e.g., for a mechanical mixture of components with different α_i's and a similar type of superposition describes the decay in a phosphor layer of such thickness that the excitation of the deeper layers differs considerably from that of the top layers. This kind of superposition has been treated repeatedly (though by no means exhaustively).

If there is an opportunity for electrons of any kind to recombine with holes left by electrons of all kinds, one may expect a system of equations of the form,

$$dn_i/dt=-\alpha_i n_i \sum_k n_k \quad (\text{again with } \sum_k n_k=N), \qquad (3)$$

to be valid. This is the form first suggested by Antonov-Romanovski[1] and analyzed by Ellickson and Parker.[2]

First, we are not quite certain that this system of equations describes adequately a plausible physical process. If the bimolecular character of the decay is due to retrapping, the rate of change of the ith kind of electrons should be described not only by a negative decay term but also by a positive retrapping term. We shall disregard these doubts, however, and assume that the system (3) describes well enough a possible decay processes. Ellickson and Parker's reasoning, simplified only by a change in notation, is essentially as follows: As usual, they assume that the emitted intensity is given by $B=-dN/dt$.

From (3) by summation over all the i's, we obtain

$$-B=dN/dt=-N\,\Sigma\,\alpha_i n_i. \qquad (4)$$

Integrating Eq. (3) with respect to t and using the abbreviation,

$$\int_0^t N(t)dt=\psi(t)$$

we obtain

$$n_i=n_{i0}e^{-\alpha_i\psi(t)}. \qquad (5)$$

At this point, Ellickson and Parker refer to graphs of their empirical curves and conclude from them that for large values of the time, $\Psi(t)$ becomes constant. No more reason than an apparent visual evidence is given. Now, it is true that for every decay curve the rate of increase of $\Psi(t)$ decreases towards 0. This does *not* necessarily mean that $\Psi(t)$ approaches asymptotically a constant value.

[a] In our first communication on infra-red-sensitive phosphors, (Urbach, Hemmendinger, and Pearlman, J. Opt. Soc. Am. 36, 372 (1946)), we derived a similar result from the same hysteresis curves by pointing out that the light-sum stored in the phosphors is of the order of the number of samarium atoms. These were shown to be responsible for the traps with the one micron absorption peak. Since the efficiency of the phosphors by stimulation is far from unity, retrapping must be assumed. The present reasoning has the advantage of not depending upon the results of the difficult absolute light-sum measurements

Substituting this constant, κ, in (5) and the resulting expression in (4), we have

$$dN/dt = -N \times \text{const.},$$

and thus an exponential decay of $N(t)$ and $B(t)$. The substitution, however, which produces this result is contradictory, since it also makes all n_i's constant and thus also $N(t)$ constant. Obviously, we cannot use, for finite positive α_i's, $\Sigma\, \alpha_i n_i$ as a constant while using in the same equation $\Sigma\, n_i$ as a variable. The asymptotic approximation used is not good enough for substitution in the exponential. This will become clearer later on.

It can be shown in fact that the asymptotic behavior of any system of the form (3) with an finite number of components is of the form, $N(t) \sim 1/t, B(t) \sim 1/t^2$. In the case of only two components, this is easily done by dividing the two equations, integrating the resulting differential equation and substituting the result in the original equations. These equations show then clearly that at sufficiently large value of the time the component with the larger value of α_i will become negligible. This reasoning can be generalized for any finite number of components; for sufficiently large values of t, only the n_i connected with the smallest α_i will contribute appreciably to the sum in (3), so that the asymptotic behavior, $1/t$, is obtained for $N(t)$.

The same "survival of the slowest component" is trivial in the case represented by the system (2), as Mott and Gurney[a] have pointed out.

At this point, however, two criticisms of our treatment must be considered: One is the comparison of what is observed experimentally for "very long times" with the asymptotic behavior of the theoretical equations. Strictly speaking, the latter can never be observed, and an uncertainty about the significance of the prolonged observation necessarily remains. (It should be noted here that ordinary measurements become impossible, and theories of the type here considered become meaningless at the point at which statistical fluctuations become appreciable.)

A more serious objection may be raised against the use of a finite number of components. It is quite possible that a continuous distribution of decay constants is far more adequate for describing the observable events. The example of superpositions of exponentials can also be adduced: With a finite number of components the survival of the slowest component would again be obtained, and thus an exponential asymptotic behavior. Only by using a continuous distribution function, as Antonov-Romanovski, and Randall and Willkins have done, is it possible to produce the form of a second-order decay, particularly its asymptotic behavior.

Therefore, we introduce the continuous counterpart of (3), replacing $n_i(t)$ by $n(\alpha, t)d\alpha$. This yields

$$[\partial n(\alpha, t)]/\partial t = -\alpha n(\alpha, t) \int_0^\infty n(\alpha, t)d\alpha. \qquad (6)^{b}$$

The integral to the right, $\int_0^\infty n d\alpha = N(t)$, is again a function of t only, as is $B(t) = -dN/dt$, and also the integral $\int_0^t N(t)dt = \Psi(t)$. Again, by definite integration, and using for the initial distribution function $n(\alpha, 0)$, the notation $n_0(\alpha)$, we get

$$n(\alpha, t) = n_0(\alpha)e^{-\alpha \Psi(t)}. \qquad (7)$$

This general form of the decay of the components (in which $\Psi(t)$ is unknown) we substitute in (6). This yields

$$N(t) = d\Psi/dt = \int_0^\infty n_0(\alpha)e^{-\alpha\psi(t)}d\alpha, \qquad (8)$$

for a large class of functions $\psi(t)$, the integral to the right is the Laplace Transform of $n_0(\alpha)$ which we may write symbolically as $\mathfrak{L}_\psi\{n_0(\alpha)\}$ and which can be obtained graphically or in closed form for any reasonable $n_0(\alpha)$. Thus (8) may be rewritten as

$$d\psi/\mathfrak{L}_\psi\{n_0(\alpha)\} = dt, \qquad (9)$$

which reduces the solution of (6) to a simple integration. Before giving an example, we may note an important property of the physically interesting solutions, for which $N(t) > 0$, and therefore $\Psi(t)$ monotonically growing, and $\lim_{t\to\infty} N(t) = 0$. Equation (9) then imposes the condition that $\Psi(t)$ must not have any upper bound. The exponential decay function does not fulfill this last condition. For an example of a solution, we use as an initial distribution function

$$n_0(\alpha) = \alpha^p e^{-\alpha c}. \qquad (10)$$

Antonov-Romanovski has shown that with exponential components, this distribution function[c] produces a decay of the general type of Becquerel's empirical formula,

$$N(t) = \int_0^\infty \alpha^p e^{-\alpha c} e^{-\alpha t} d\alpha = \mathfrak{L}_t\{\alpha^p e^{-\alpha c}\} = \frac{\Gamma(p+1)}{(c+t)^{p+1}}. \qquad (11)$$

The exponent in the denominator has only the limitation $p > -1$; there seems to be no obvious reason why $p = 0$ should be of particular significance, and why p should not have large positive values representing power laws with high powers which have never been observed. In our case, the distribution function (10) leads to the differential equation,

$$(c+\psi)^{p+1}d\psi = \Gamma(p+1)dt. \qquad (12)$$

The solution of which yields for $N(t)$

$$N(t) = (p+2)^{1/p+2}\{\Gamma(p+1) \times t + K\}^{-p+1/p+2}\Gamma(p+1), \qquad (13)$$

where K is an integration constant. This solution is again of the Becquerel form,

$$N(t) = c_1/(c_2+t)^p, \qquad (14)$$

but the exponent in the denominator depends now upon the power p in the distribution (10) in a very different and much more plausible manner: Although p has again no upper limit, the value of P is now limited, $0 < P < 1$, and if the exponent in (10) is large enough, the asymptotic behavior of the solution will approach $1/t$ to any desired extent.

The above example has been selected not only because of the interesting comparison with the superposition of exponentials, but also because the last result may be greatly generalized. On the basis of a theorem in the general theory of Laplace transforms,[d] it can be shown that for any distribution function which behaves in a neighborhood of zero like α^p, the asymptotic behavior for large values of t is of the form (13). In other words, the more rapidly n_0 approaches 0, the more closely does the asymptotic behavior of the decay approach that of a simple second-order decay. A more detailed discussion of (6) and its solutions would require an undue amount of space. The main purpose of this appendix was to prove that the observed decay is not incompatible with a superposition of bimolecular decays of the form (3) or (6).

[a] H. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940).

[b] The following treatment of the integro-differential equation, (6), was suggested by Dr. W. Seidel, of the University of Rochester. To him and to Mr. R. C. Gosselin we are greatly indebted for much mathematical help and advice. A detailed discussion of (6) was the subject of Mr. Gosselin's Master's thesis at the University of Rochester.

[c] The corresponding trap depth distribution with constant rate factors would be of the form

$$e^{-\epsilon/T}[\exp(-cse^{-\epsilon/T})].$$

[d] Cf. Doetsch, *Theorie und Anwendung der Laplace Transformation* (Dover Publications, New York, 1943), p. 200.

A Correlation between Cathodoluminescence Efficiency and Decay as a Function of Temperature*

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An investigation of the temperature variation of the cathodoluminescence efficiency of a manganese-activated zinc-fluoride phosphor (tetragonal-ZnF_2·0.005Mn) revealed a pronounced secondary increase in efficiency when the temperature was raised above 210° to about 330°C. This efficiency increase was accompanied by an intensity increase in the power-law-decay "tail" through that temperature range. The rapid emptying of traps at these temperatures, followed by radiative transitions of the freed electrons, can account for both observed results. Similar effects were found for a manganese-activated zinc-sulfide phosphor (hexagonal-ZnS·0.018Mn), and for a copper-activated zinc-cadmium-sulfide phosphor (hexagonal-9ZnS·CdS·0.0001Cu). All measurements were made on aluminum-backed phosphor screens in sealed-off cathode-ray tubes. Decays were measured by photographing the output of a multiplier photo-tube as recorded on a d.c. oscilloscope.

INTRODUCTION

THE temperature dependence of the luminescence efficiency and decay characteristics of phosphors has been widely used as a means of investigating the mechanism of luminescence.[1] The variation of efficiency with temperature has been used to interpret the observed luminescence for several exponential-decay phosphors as the result of a competition between a radiative, non-temperature-dependent process and a dissipative, highly temperature-dependent process.[2,3] This interpretation explains the rapid decrease in efficiency in a relatively short temperature interval beyond a certain critical temperature. It furthermore predicts a close relationship between efficiency and the observed rate of decay, this being a completely reciprocal one in the ideal case. Only decay curves of exponential form may be directly interpreted in this way, but decay curves of power-law form are useful for the information they contain concerning the emptying of traps in the phosphor; it being understood that this pertains insofar as the freed electrons undergo radiative transitions. An electron in a trap may be considered as an electron in a metastable state, release from which requires a certain amount of activation energy, called the trap "depth." Electrons which are trapped in shallow traps, i.e., shallow with respect to the thermal energy (kT) available at the temperature of operation, will contribute predominantly to the phosphorescence emission at short times of decay, whereas the contribution of those in deeper traps will become apparent at longer times.

This paper describes measurements of the temperature dependence of efficiency and decay between 25° and 300°C for three phosphors: two of the exponential-decay type with power-law decay at long times (called "tails"), and one of completely power-law decay type, under cathode-ray excitation. The results show a correlation between the appearance of a secondary efficiency maximum and an increase in intensity of the decay-"tails" with increasing temperature, and are analogous to those reported by Shrader[4] for phosphors with very deep traps under excitation by ultraviolet light.

APPARATUS AND PROCEDURE

The materials and measuring equipment used were devised and provided by members of the chemico-physics section of the RCA Laboratories Division. A layer of the phosphor to be tested was settled from aqueous suspension onto a glass disk. An electron-permeable light-reflecting aluminum backing was evapo-

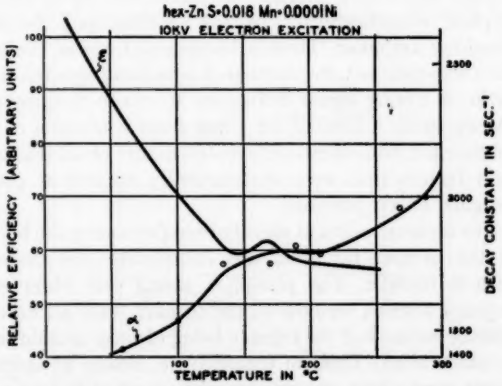

FIG. 1. Relative efficiency $\mathcal{E}$ and observed initial decay "constant" α as a function of operating temperature for hexagonal-ZnS·0.018Mn(Ni).

* Presented at the meeting of the Optical Society of America, March 10, 1949. Work done under Contract N6onr-236 between ONR and RCA.

[1] For a comprehensive index of publications dealing with these subjects, reference should be made to H. W. Leverenz, *Introduction to the Luminescence of Solids* (John Wiley & Sons, Inc., New York), in press. Energy-level diagrams pertinent to the results described in this paper are given in H. W. Leverenz, "Luminescent solids (phosphors)," Science **109**, No. 2826, 183–195 (February 25, 1949).

[2] N. F. Mott and R. W. Gurney, "Luminescence in solids," Trans. Faraday Soc. (1938).

[3] F. A. Kroeger *et al.*, Physica **14**, 81 (1948).

[4] R. E. Shrader, H. W. Leverenz, and E. J. Wood, J. Opt. Soc. Am. **36**, 353 (1946).

TABLE I. A summary of the experimental results showing a correlation between the temperature ranges wherein luminescence efficiency and phosphorescence intensity (decay-"tail") increase.

Phosphor	Temperature range of efficiency increase	Maximum efficiency increase	Temperature range of "tail" increase	Maximum "tail" increase
Tetragonal-ZnF_2:Mn	210°–>330°C	>42%	150°–290°C	206%
Hexagonal-9ZnS·CdS:Cu (blue emission band)	130°–150°C	19%	100°–240°C	124%
Hexagonal-ZnS:Mn:Ni	145°–165°C	4%	145°–190°C	11%

rated over the resultant phosphor screen.[5] Screen densities were about 4 mg/cm², and the aluminum backing was about 1000A thick, i.e., about 80 percent of 10-kv primary electrons penetrate the aluminum. The phosphor screens were mounted in sealed-off cathode-ray tubes designed by S. Lasof. A stationary unmodulated defocused cathode-ray beam delivering about 1 μa/cm² was used in each case. Measurements were made on two of the tubes with 10-kv electron excitation and 15 kv was used on the third (that containing tetragonal-ZnF_2:Mn) because of adverse secondary emission characteristics from the aluminum at the lower voltage. Account was taken of the secondary emission from the aluminum backing in determing the true current to the screen. A metal diaphragm, electrically connected to the second anode of the tube, was mounted just behind the screen to limit the cross section area of the defocused electron beam.

The light output from the screen was detected by a multiplier photo-tube (RCA 1P28) attached either to a sensitive microammeter for efficiency measurements or to the vertical deflection of a d.c. oscilloscope for observing decays. In the latter case, the horizontal sweep of the oscilloscope was synchronized with a suitable timing signal from an audio oscillator, this signal being applied simultaneously to the oscilloscope's beam-blanking amplifier. Thus, a horizontal trace of timing dots was obtained, the number of dots being equal to the ratio of timing signal frequency to sweep frequency. Decays were measured for times from a fraction of a millisecond to several seconds by means of increasing gain factors that were automatically applied at pre-assigned sweep positions.

For measurements at elevated temperatures, the bulb of the cathode-ray tube was completely surrounded with a furnace. The phosphor screen was observed through a small window in the furnace wall, all other interior surfaces of the furnace being of sheet aluminum at substantially uniform temperature. Before measurements were taken, special care was exercised to insure that temperature equilibrium was established.

[5] D. W. Epstein and L. Pensak, "Improved cathode-ray tubes with metal-backed luminescent screens," RCA Review VII, No. 1, 5–11 (March, 1946).

RESULTS

A summary of the experimental results is shown in Table I. Throughout this paper only relative values of efficiency are presented, corresponding to the ratio of light output of the phosphor screen *during excitation* to the power input of the electron beam. The percent increases in decay-"tail" intensity *after excitation* are measured in terms of the times at which the intensity of phosphorescence emission has decreased to an assigned fraction of its initial value. It may be observed that the temperature ranges for increase in luminescence efficiency and intensity of decay-"tail" either coincide or overlap to a large extent.

Figure 1 is a plot of relative efficiency $\mathcal{E}$ and observed initial decay "constant" α, i.e., the slope of the initial exponential decay, as a function of temperature for the hexagonal-ZnS·0.018Mn phosphor under 10-kv electron excitation. A secondary maximum of efficiency is found at about 170°C, together with a considerable departure from the previous rate of decrease both before and after this temperature. The presence of a secondary efficiency maximum has been reported for a ZnS:Mn phosphor by Brauer.[6] The small amount of Ni in the sample** used here has an inappreciable effect on the decay curve. In the variation of α, a minimum is found in the neighborhood of 200°C. An examination of the individual curves (Fig. 2) from which these values of α were obtained, showing also the decay-"tails," reveals that the curves between 134° and 233°C are practically identical. Closer

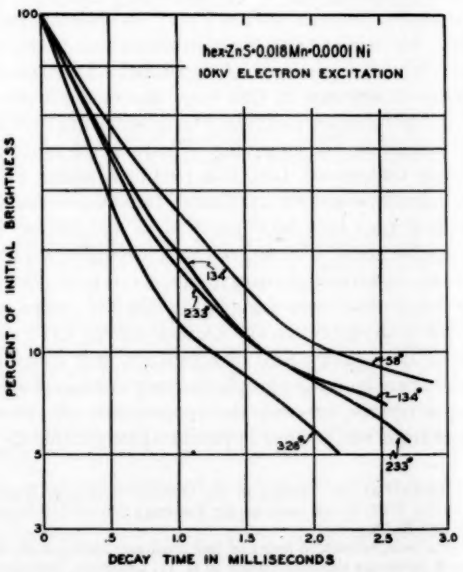

FIG. 2. Cathodophosphorescence decay curves for hexagonal-ZnS·0.018Mn(Ni).

[6] P. Brauer, P.B. 19206 (1944).

** This sample was synthesized by Dr. A. L. Smith, RCA, Victor Division, Lancaster, Pennsylvania.

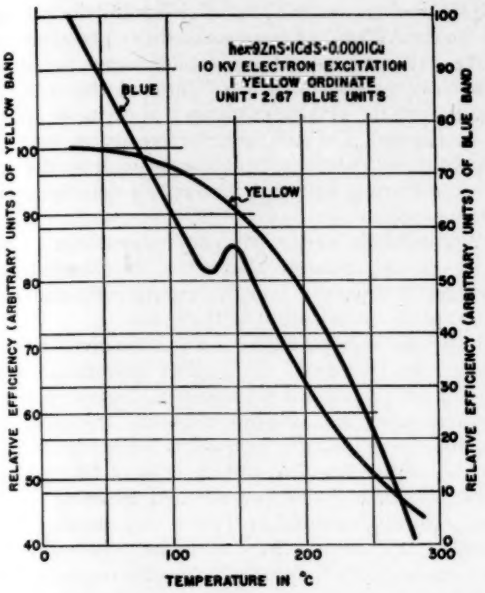

FIG. 3. Relative efficiency $\mathcal{E}$ for the blue and yellow emission bands of hexagonal-9ZnS·CdS·0.0001Cu as a function of operating temperature.

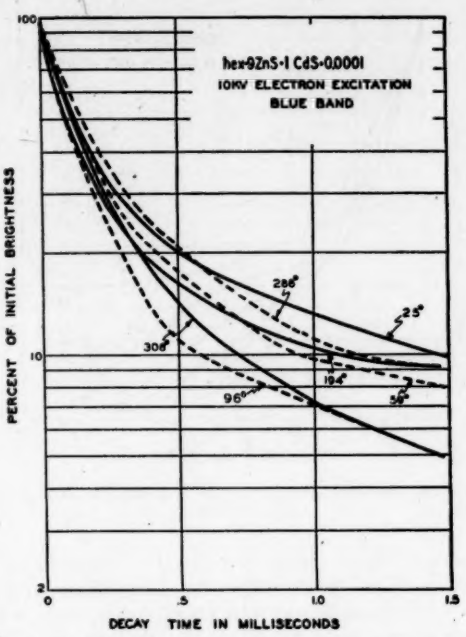

FIG. 4. Cathodophosphorescence decay curves for hexagonal-9ZnS·CdS·0.0001Cu.

inspection of other decay curves within this region, not shown in the figure, shows that the curve for 209° lies above that for 190°C.

The luminescence output of the hexagonal-9ZnS·CdS·0.0001Cu phosphor (Figs. 3 and 4) consists of a blue and a yellow emission band. These bands were detected separately by using appropriate filters. As the operating temperature is increased, the yellow band, due to the Cu, exhibits decreasing efficiency and phosphorescence intensity. But the blue band, characteristic of hexagonal-9ZnS·CdS without added activator, exhibits irregularities. It has a secondary efficiency maximum at about 150°C and the intensity of the latter stages of phosphorescence reverses its normal behavior and increases in the temperature range from 96° to 286°C.

The largest effect of this type was found for the tetragonal-ZnF_2·0.005Mn phosphor (Figs. 5 and 6). The efficiency decreases slowly to about 210°C and then rises to a maximum located beyond 300°C. Here, also, the intensity of the decay-"tail" increases in the temperature range of 142° to 280°C.

CONCLUSIONS

The general theory of trapping, applied to the case of these three examples, can explain why a secondary efficiency maximum and an increase in intensity of the decay-"tails" of exponential-decay phosphors or of the latter stages of phosphorescence of power-law-decay phosphors appear together. This is done by assuming that the rapid emptying of traps at a certain operating temperature, during which the freed electrons undergo radiative transitions, causes a secondary efficiency maximum to appear. The exhibition by a phosphor of such a secondary efficiency maximum and concomitant increase in decay-"tail" or phosphorescence intensity may be thought of in the following way: There may be present in the phosphor either shallow traps, all of which will empty rapidly at some temperature less than a given temperature T, or no traps at all which will empty rapidly at a temperature less than T, and there must be deep traps which will empty rapidly only at or above T. If shallow traps are present, they may be detected for

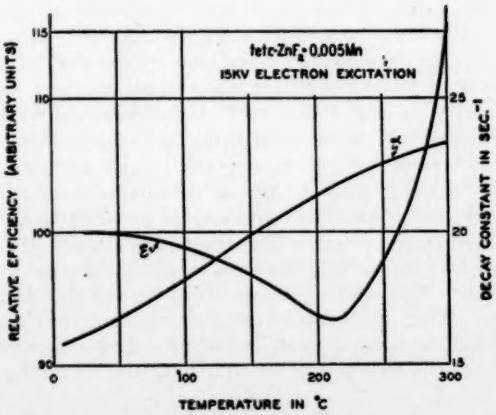

FIG. 5. Relative efficiency $\mathcal{E}$ and observed initial decay "constant" α as a function of operating temperature for tetragonal-ZnF_2·0.005Mn.

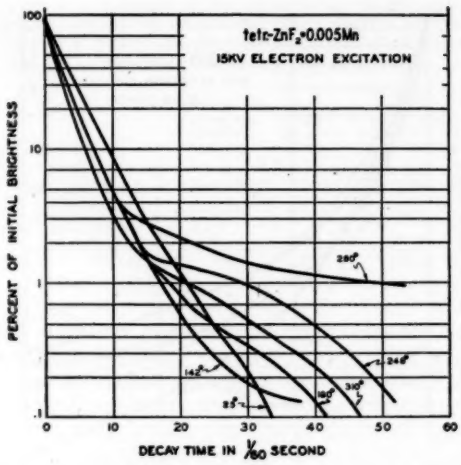

FIG. 6. Cathodophosphorescence decay curves for tetragonal-ZnF_2·0.005Mn.

exponential-decay phosphors by the presence of a decay-"tail" at temperatures less than T but greater than a minimum temperature which corresponds to the lowest temperature at which the shallow traps will empty at a measurable rate. Shallow traps will likewise be observable if present in power-law-decay phosphors by causing an appreciable phosphorescence over a similar temperature range. Their presence is not necessary for the appearance of the secondary efficiency maximum, but they seem to be present in the phosphors tested. For temperatures between the lowest temperature at which shallow traps empty rapidly and T, a certain proportion of the excited electrons will be caught in deep traps, and a corresponding number of centers are rendered effectively inactive. As the temperature is increased through this same range, there will be an increasing probability of excited electrons making dissipative (non-radiative) transitions because thermal agitation generally interferes with luminescence, and therefore the observed efficiency will decrease. At the same time, the observed initial decay "constant" of an exponential-decay phosphor will increase, and both the intensity of the decay-"tail" for exponential-decay phosphors and of the latter stages of phosphorescence for power-law-decay phosphors will decrease because of a decreasing probability for electrons to be trapped in the shallow traps. This assumes that contributions to the power-law-decay in this temperature range come only from the shallow traps, as would be the case for sufficient difference in the depths of shallow and deep traps. When the temperature T is reached, the deep traps begin to empty at an appreciable rate and more of the centers become available for repetitive excitation. On continuing to raise T, the efficiency and the intensity of the decay-"tail" of exponential-decay phosphors and of the latter stages of the phosphorescence for power-law-decay phosphors increase until all the traps are empty and the maximum number of excitable centers is approached. For still higher temperatures, both the efficiency and the intensity of power-law-decay decrease because thermal agitation increasingly interferes with luminescence.

Whenever a secondary efficiency maximum or a maximum at temperatures above 0°K is observed, the presence of traps which empty rapidly near that temperature should be sought as the cause.

If the rate of emptying for N traps of a given depth is N/sec., the trap depth E^* is given approximately by $E^* = (\ln s)kT$, where $\ln s$ is the natural logarithm of the thermally produced attempt-to-escape frequency for electrons in traps; this frequency being reported by Randall and Wilkins[7] to be of the order of $10^{8\pm1}$ per sec. Using a value of $s = 10^8$ per sec., and assuming s to be practically independent of T, the trap depths which produce the observed effects are found to be 0.67 ev for the hexagonal-9ZnS·CdS:Cu, 0.70 ev for the hexagonal-ZnS:Mn, and about 1 ev for the tetragonal-ZnF_2:Mn phosphors investigated. From a study of the thermostimulated luminescence of another sample of tetragonal-ZnF_2:Mn, a trap depth of about 1 ev has been reported by Johnson and Williams.[8] Experiments in these laboratories have shown that the composition and conditions of synthesis of this type of phosphor greatly affect its electron trapping characteristics.

The fact that the yellow emission band of the hexagonal-9ZnS·CdS:Cu phosphor does not show a secondary efficiency maximum and a region of increasing phosphorescence intensity, although the blue emission band does, indicates that traps responsible for the behavior of the latter are associated only with the blue luminescence centers in this phosphor.

Although screens of phosphors of this type exhibit a small hysteresis in their $\mathcal{E}$ *vs.* T curves upon heating and cathode-ray bombardment (even at the moderate current densities used), the results are reproducible. The actual measured locations of the secondary maxima may, however, vary by ±10°K.

ACKNOWLEDGMENTS

The author wishes to express his appreciation for the guidance of S. Lasof in the beginning of this work, and to H. W. Leverenz and Dr. R. E. Shrader for their constant interest and valuable suggestions.

[7] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. **184**, 390 (1945).

[8] J. S. Johnson and F. E. Williams, J. Opt. Soc. Am. **39**, 709 (1949).

The Phosphorescence Decay of Halophosphates and Other Doubly Activated Phosphors

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The decay rates of three doubly activated phosphors, namely, calcium halophosphate (Mn, Sb), calcium silicate (Mn, Pb), and zinc fluoride (Mn, Ti, or W) have been investigated under λ2537 excitation. The halophosphates studied all show initially a very rapid and abrupt decay, followed by a second stage of decay having a very slow rate. Both stages are of the exponential type. Investigation shows that the rapid rate (decay constant ≈ 1500 sec.$^{-1}$) is to be ascribed to the antimony emission and the slow rate ($k \approx 75$ sec.$^{-1}$) to the manganese emission.

Calcium silicate behaves in a similar fashion, the ultraviolet emission due to lead decaying rapidly ($k \approx 480$ sec.$^{-1}$) and the visible more slowly ($k \approx 60$ sec.$^{-1}$). The doubly activated zinc fluorides show similar behavior, though the great spectral width of the tungsten band makes separation of the two emission bands difficult.

The fact that in all these cases, the two activators each retain their characteristic decay rates in the presence of the other indicates that two types of centers exist in each of which the process of luminescence functions independently of the other.

INTRODUCTION

In recent years a considerable number of doubly activated phosphors have been developed and their optical properties studied. They are of two classes. One is the infra-red sensitive phosphor in which the role of the secondary activator is to make possible a storage of luminescence energy by such deep traps that it can be released only by stimulation with infra-red. Their phosphorescence is, in general, temperature sensitive and can be ascribed to the introduction of traps.

The second class includes those in which a secondary activator is added for the purpose of sensitizing the emission of the primary activator to a specific spectral range of excitation. It has acquired attention not only from its scientific interest, but also because it affords a means of developing new phosphors for application to the fluorescent lamp whose operation depends upon excitation by λ2537, the predominant line in the low pressure mercury discharge. In the phosphors of this class, there is always more or less phosphorescence due to traps, but their outstanding phosphorescence is of the temperature-insensitive type exhibiting an exponential decay.

Measurements of this type of decay have previously been confined to singly activated phosphors. The present investigation was undertaken to acquire some insight as to what happens in the presence of a sensitizing activator. Three phosphors were chosen on the basis of their current interest, the calcium halophosphates, calcium silicates, and zinc fluorides.

METHOD OF MEASUREMENT

The apparatus used for the decay measurements was the same as used previously by Fonda,[1] and is represented in cross-section view Fig. 1. The phosphor was painted on a glass slide and mounted between two rotating disks. A slit in the first disk admitted light from a d.c. operated germicidal lamp (λ2537 emission) which excited the phosphor. Visible light emitted by the phosphor in turn passed through the glass slide and another slit in the second disk. The first slit could be displaced at different distances from the second, thus allowing a series of time intervals between excitation and measurement of light emitted from the phosphor. A sensitive galvanometer was used with an electron multiplier photo-tube for intensity measurement.

A Corning glass filter No. 9863 was placed between the exciting lamp and the phosphor slide to eliminate visible light originating from the germicidal lamp. This filter, when new, has approximately 50 percent transmission at λ2537.

Because of light from the exciting lamp which is transmitted by the phosphor slide when the two slits are opposite each other, a correction must be made for the zero time measurement, by subtracting the intensity registered when the slide is reversed. In this position the glass slide faces the exciting lamp, preventing the excitation of the phosphor by λ2537 radiation. In order to analyze the light emitted from the phosphor, several filters were used in front of the photo-multiplier. Corning filter No. 3389 allowed 88 percent transmission above 4200A, and No. 3486 above 5200A. Both showed negligible transmission below the respective wavelength limits indicated. A Wratten filter No. 48 allowed a maximum of 40 percent transmission at 4600A limiting transmitted light between 4000 and 5100A. The near

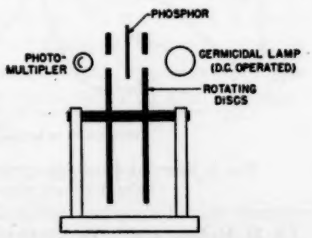

FIG. 1. Cross-sectional view of arrangement for measuring decay of luminescence.

[1] G. R. Fonda, J. App. Phys. **10**, 408 (1939).

ultraviolet region could be studied with Wratten filter No. 35 which does not transmit in the visible beyond 4100A.

CALCIUM HALOPHOSPHATES

The calcium halophosphates possess several points of interest. They represent, for one thing, a new base material for phosphors, a double compound of phosphate and halide similar to the naturally occurring mineral apatite. They represent also a particularly interesting case of photo-sensitization. When manganese alone is introduced as an activator, the resulting phosphor is responsive to excitation by cathode rays, but shows only a very weak emission in the orange red under radiation by λ2537. When antimony is added in addition to manganese, it sensitizes the emission of the latter and also introduces a distinct emission band of its own, as described by McKeag and Ranby.[2] Thus, two emission bands appear, an antimony band in the blue and a manganese band in the orange red.

We have measured the phosphorescence decay of a number of these phosphors as prepared by Dr. H. C. Froelich of Nela Park, and find them all alike in showing initially a very rapid and abrupt decay, followed by a second stage of decay having a very slow rate. Both stages of decay are of the exponential type. Scrutiny of the results discloses that the rapid rate is to be ascribed to the antimony emission, and the slow rate to the manganese.

Four typical ones have been selected for detailed description here. They differ from one another in composition and therefore also in the relative intensity of the two emission bands in the fluorescence spectrum. Their variation in spectral distribution at room temperature is shown in Fig. 2. When measured at the temperature of liquid nitrogen, each band was found to be displaced toward longer wave-length. This typical effect is illustrated for one of the phosphors in Fig. 3.

In Fig. 4 there are given curves for the decay of a

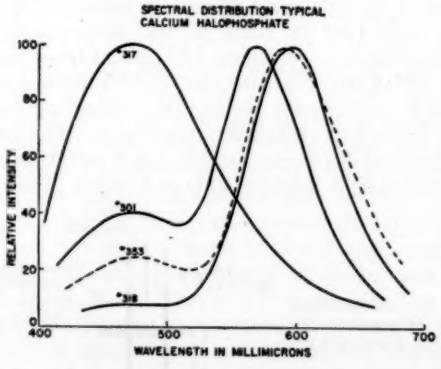

FIG. 2. Spectral distribution curves of some typical halophosphate phosphors.

[2] A. H. McKeag and P. W. Ranby, Ind. Chem. 23, 597 (1947).

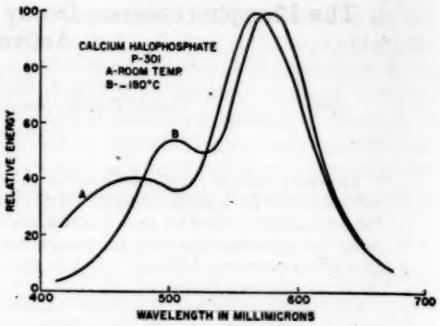

FIG. 3. Spectral distribution of typical halophosphate at room temperature and at liquid-nitrogen temperature.

halophosphate No. P-301, a phosphor whose composition lies within the range generally used, with the antimony and the manganese contents so balanced that the emission band of each is present at a significant intensity. Curve A, made with no filter between the phosphor and the photo-cell, shows the characteristic duplex decay. The initial rapid decay was segregated by interposing a filter No. 48 which transmitted only the blue luminescence of the antimony emission band and absorbed the orange-red manganese band. The result, as shown in curve C, indicates that the rapid decay of the antimony emission is of the exponential type.

A similar attempt to segregate the manganese band was made by interposing filter No. 3486, which transmits the visible above 5200A. The resulting curve B demonstrates that this was not entirely successful. The

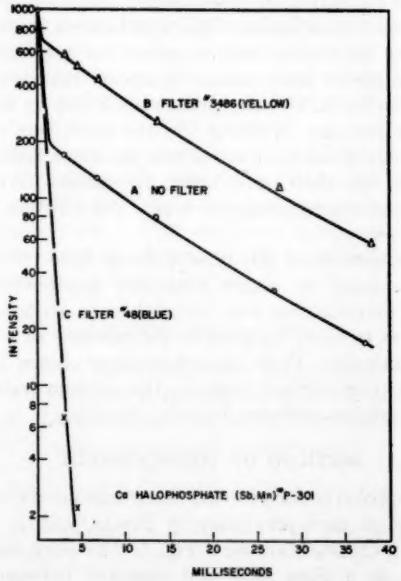

FIG. 4. Decay curves for halophosphate P-301, a phosphor whose composition lies within the range generally used in fluorescent lamps.

antimony band evidently extends to sufficiently long wave-lengths so that part of it is transmitted by the filter.

A comparison of the three curves makes clear, however, that the rapid decay is to be ascribed to the antimony emission and the slow decay to the manganese. After 15 milliseconds, the decay curve as plotted on semilog paper, begins to bend upward. This denotes that the trapped type of phosphorescence is also present. In fact, when the phosphorescence decay is viewed directly with the eye, it is this latter type only which is perceived because of its long persistence.

The curves of Fig. 5 show the decay characteristic for phosphors in which either antimony or manganese predominates. Curve A gives the results for No. P-317, containing antimony only. Even when measured directly, without filters, the rapid decay is very evidently the only type of phosphorescence present. It is therefore conclusive that this decay is to be ascribed to antimony.

In phosphor P-318 the manganese does indeed predominate but a little antimony had of necessity been introduced for the purpose of sensitizing. The antimony band, as shown in Fig. 2, is very weak. Nevertheless, it is sufficient, as shown in curve B, to produce initially a rapid drop in intensity, well pronounced even though much less extensive than from phosphors containing the normal amount of antimony. When the filter No. 3486 was interposed, the blue antimony band was completely absorbed, so that the resulting curve C portrays, throughout its course, the decay of the manganese band, back to zero time.

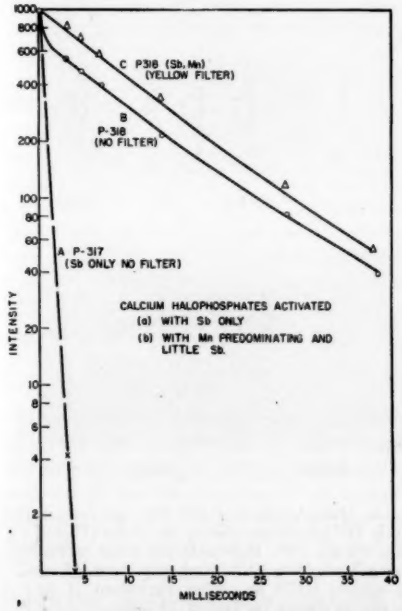

FIG. 5. Decay curves for halophosphates in which either antimony or manganese predominates.

TABLE I. Decay of calcium halophosphates containing variable amounts of antimony and manganese.

No.	Composition	Relative emission Sb	Height bands Mn	Decay in phosphorescence: Initial decrease	K_{Sb}	K_{Mn}
P-301	Normal range	20	100	80%	1500 sec.$^{-1}$	75 sec.$^{-1}$
P-353	Normal range	12	100	80	—	75
P-318	Low Sb, High Mn	4	100	30	—	82
P-317	Sb only, no Mn	100	0		1700	—

Results on the four phosphors are summarized in Table I. Under the heading "Initial decrease in phosphorescence" are recorded values which indicate the extent to which the decay of the antimony emission band contributes to the decay of the over-all emission. They are derived from the decay curves obtained without filters by extrapolating back to zero time the straight line reproducing the manganese decay and then by expressing the percentage which this light intensity bears to the total intensity actually observed at zero time. If manganese had conceivably been present alone, the value for this expression would of course have been zero.

Tests have been made by W. B. Goad, Jr., formerly of this laboratory, on the flicker from individual phosphors when introduced as coatings for a.c. lamps of the fluorescent type. Under a rapid succession of pulse excitations, such as occurs with 60-cycle operation, the intensity of the light emitted by a phosphor is diminished somewhat between peaks of the a.c. waves. The extent of the reduction is a function of the rate of decay. The flicker observed from a lamp is a measure of this extent. According to Mr. Goad's measurements, the amount of flicker from a calcium halophosphate having approximately the composition and characteristics of P-301 was double that of the zinc silicate type activated with manganese alone. The explanation of this apparent discrepancy is offered by our present measurements which bring out the role played by the antimony in greatly accelerating the initial rate of decay which is the controlling factor in developing flicker.

We have not examined in detail the trapped type of phosphorescence for the halophosphates, but we believe it would be remunerative to measure glow curves and the contributions made to them by each activator. A striking effect is observable in a phosphor which has been cooled in liquid nitrogen and then allowed to warm up. At a temperature not far above that of liquid nitrogen, the blue glow of antimony appears, even in the presence of manganese. This indicates that the shallowest traps are the ones associated with the phosphorescence of antimony.

CALCIUM SILICATE

A calcium silicate phosphor, activated with manganese and sensitized to λ2537 with lead, has been de-

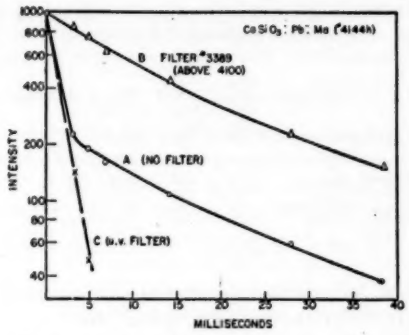

FIG. 6. Decay curves for calcium silicate (Pb, Mn) phosphor.

scribed by Froelich.[3] It differs from the halophosphates in that the emission band of the sensitizing agent, lead, lies in the ultraviolet, with a peak near 3400A, instead of in the visible. The manganese emission lies in the orange red.

The type of recording cell used is responsive to the ultraviolet as well as to the visible. Consequently, the decay of both ultraviolet and orange bands could be measured. The results are essentially similar to those observed with the halophosphates. They are shown in the curves of Fig. 6.

Curve A is based on measurements made without any filter. The initial abrupt decay is that of the ultraviolet lead band. This was proved by repeating the measurement recorded in curve C, with filter No. 35, which transmits the near ultraviolet and absorbs the visible. That the slow stage of decay is that of the orange manganese band is shown by the course of curve B, made with filter No. 3389, which absorbs the ultraviolet.

The decay constant for the Pb band is approximately 480 sec.$^{-1}$ and for the Mn band 60 sec.$^{-1}$.

As the manganese band is the only one observed visually, curve B portrays correctly the performance of the phosphor in lamps under 60-cycle operation. The flicker is about the same as from zinc silicate phosphors activated with manganese alone.

Spectrograms of the fluorescence and phosphorescence are shown in Fig. 7. A and B give the spectra of the luminescence of the halophosphate P-301, taken 6 milliseconds after excitation, and at the instant of excitation, respectively, using a glass spectrograph, and it shows the early decay of the antimony band. In C and D are shown the spectra of calcium silicate (Pb, Mn), 40 seconds after excitation and during excitation, respectively, taken with a small quartz instrument. This substantiates the rapid decay of the lead band.

By contrast with the different decay rates for the bands due to the sensitizer and the manganese in these phosphors, it is of interest to note that the two overlapping bands due to manganese alone, both in calcium silicate (Pb, low Mn) and zinc beryllium silicate appear, as far as can be judged from spectrum photographs, to decay at the same rate. Figure 7, E and F are spectrograms of the phosphorescence and fluorescence of a zinc beryllium silicate phosphor whose spectral distribution curve clearly shows two overlapping bands. The identical appearance of the original spectrograms indicates that there is no differential decay rate for the two bands.

ZINC FLUORIDE PHOSPHORS

The characteristics of these phosphors when activated with manganese alone have been described by Williams and Eyring.[4] This phosphor is responsive to cathode rays, but is only weakly excited by λ2537. Either tungsten or titanium serve, however, to sensitize it to

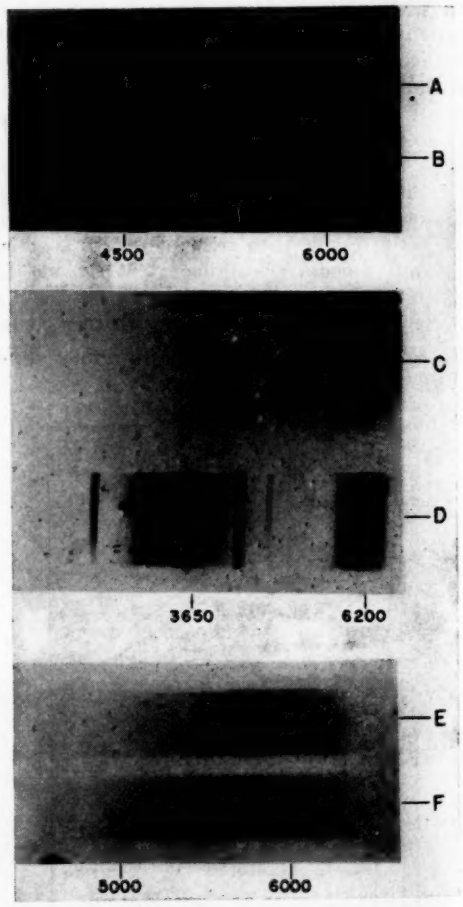

FIG. 7. A. Halophosphate 0.006 sec. after excitation (8-hr. exposure). B. Halophosphate during excitation (15-min. exposure). C. Calcium silicate (Mn, Pb) 0.035 sec. after excitation (5 hr.). D. Calcium silicate (Mn, Pb) during excitation (15 min.). E. Zinc beryllium silicate 0.025 sec. after excitation (7 hr.). F. Zinc beryllium silicate during excitation (15 min.).

[3] H. C. Froelich, J. Electrochem. Soc. **93**, 101 (1948).

[4] F. E. Williams and H. Eyring, J. Chem. Phys. **15**, 289 (1947).

TABLE II. Decay of zinc fluoride phosphors.

Phosphor	Filter	K_W	K_{Ti}	K_{Mn}
ZnF_2:W:Mn (No. 3010)	No. 3486	—	—	13.8 sec.$^{-1}$
ZnF_2:W (No. 3048)	none	>1600	—	—
ZnF_2:Ti:Mn (No. 3098)	none	—	—	13.8
ZnF_2:Ti (No. 3007)	No. 3486	—	50 sec.$^{-1}$	13.8

λ2537.[5] Tungsten by itself gives a very weak whitish emission; titanium alone, a weak orange, very broad, with its peak at about the same position as that of the manganese band.

The tungsten emission was so weak and its decay so rapid that it was difficult to record accurately more than the initial intensity of its luminescence. Satisfactory measurements could be made with the other activators, facilitated by the slow decay of titanium alone. The decay of manganese band was already known to be extremely slow. The results are given in the curves of Fig. 8 and in Table II.

In phosphors containing tungsten and manganese as dual activators there is an initial steep drop in decay that is to be ascribed to the very rapid decay of the tungsten band. Such results as we could measure with tungsten alone demonstrated that this rate is higher than 1600 sec.$^{-1}$. The tungsten band is of such broad spectral width that it is transmitted even by the filter No. 3486, which absorbs below 5200A. Consequently, the initial drop in decay was recorded even when this filter was used, as illustrated by curve A.

With titanium alone there was a moderate initial drop in the decay curve that persisted even with filter No. 3486 as shown in curve C. This seems significant, for it indicates that the extraordinary broad emission band of titanium[5] may be, in fact, an aggregate of two bands, the shorter of which is characterized by a relatively greater rate of decay.

In phosphors containing both titanium and manganese, it has already been proved that the emission of titanium is completely suppressed by the manganese. This accounts for the character of its decay, as illustrated in curve B, which shows the extremely slow decay rate characteristic of manganese to be maintained right back to zero time. The decay rate which we find for manganese, 13.8 sec.$^{-1}$, is in fair agreement with the value of 11.5 sec.$^{-1}$ reported by Williams and Eyring for cathode-ray excitation.[4]

DISCUSSION

The halophosphates and the calcium silicate phosphors offer the greater interest for two reasons. Each activator employed, for one thing, introduces an emission band whose spectral location is so separate from the others and whose intensity is so strong that there is no difficulty in segregating it and in recording its decay. For another thing, the rates of decay of each element in a pair of activators are so radically different

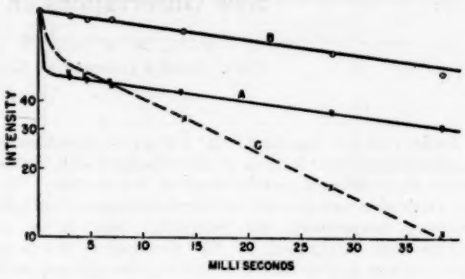

FIG. 8. Decay curves for zinc fluoride phosphors. A. ZnF_2 (W, Mn) $K_{Mn}=13.8$ sec.$^{-1}$ using filter No. 3486 transmitting above 5200A. B. ZnF_2 (Ti, Mn) $K_{Mn}=13.8$ sec.$^{-1}$ measured with no filter and also with filter No. 3486. C. ZnF_2(Ti) $K_{Ti}=50$ sec.$^{-1}$ measured with filter No. 3486.

that recording is still further facilitated. There can, therefore, be no ambiguity in the observations which showed beyond doubt that the exponential decay of each activator persists independently of the other.

This result appears significant in the theory of luminescence in that it lends support to Williams' hypothesis for the mechanism of fluorescence emission from phosphors of the silicate type.[6] He has shown that the energy relationships are such that this emission may be ascribed to the release of an electron from an upper excitation state. Now, the temperature-insensitive type of decay, such as is represented by the decay measurements described above, cannot be associated with traps. Rather, it is of the nature of an afterglow of fluorescence and therefore intimately connected, as Williams believes, with the mechanism of fluorescence. That it occurs at a finite and measurable rate is an indication that the release of electrons from the uppermost excitation state is probability phenomenon. This state, in other words, partakes of the nature of a metastable condition except that it possesses a greater or smaller probability for the release of electrons to the excitation state of lower energy content.

In the halophosphates, for instance, the probability for release of excited electrons belonging to antimony centers, to use the term coined by Lenard, would be very much greater than that characteristic of manganese centers.

To find, therefore, that two activators each retain their characteristic decay rates in the presence of the other, tends to substantiate the conception of an activator center as a system associated with a specific activator. When two activators are present, two types of centers will exist in each of which the process of luminescence functions independently of the other.

The authors wish to express their appreciation to Dr. G. R. Fonda of this laboratory for many helpful suggestions and to Dr. H. C. Froelich of Nela Park who furnished us with a number of the phosphors studied.

[5] G. R. Fonda and F. J. Studer, J. Opt. Soc. Am. 12, 1007 (1948).

[6] F. E. Williams, Phys. Rev. 73, 1257 (1948).

New Observations on Superlinear Luminescence*,†

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(Received May 2, 1949)

In earlier papers it was shown that a group of phosphors show an approximately linear increase of their efficiency with increasing intensity of excitation in certain ranges of that intensity. Tentatively, these observations and the interdependence of the effects of intensity, temperature, and "poisoning" found in the same phosphors were interpreted by the assumption that a non-radiative process of first-order kinetics competes with an emission process of the second order. This type of hypothesis, however, does not easily account for more than linear dependences of efficiency on intensity. Indications of such dependences had been found in our earlier work. In view of the possible theoretical significance of these results, a number of measures were taken to eliminate possible sources of errors. New measurements were carried out on a suitable series of poisoned zinc-cadmium sulfide phosphors. The existence of regions in which the intensity dependence of efficiency was even stronger than quadratic was ascertained. Furthermore, a remarkably strong dependence of the efficiency on the carefully controlled concentrations of the poison was found. The problems raised by these effects are briefly discussed.

At earlier meetings of this Society[1,2] we communicated and demonstrated observations showing that the efficiency of certain phosphors increased very rapidly with an increase of exciting intensity. We tried, then, to interpret this phenomenon in the simplest possible terms. In ordinary luminescence of less than 100 percent efficiency, the percentage of radiationless processes is constant, independent of intensity. Our observations showed that in certain zinc sulfide-type phosphors the radiationless transitions were markedly preponderant at low intensity, but that when the intensities increased, the percentage of radiative transitions increased rapidly. If both processes depend, as they certainly must, upon the concentration of excited states, this dependence must be much stronger for the radiative process than for the competing non-radiative one. It appeared plausible to assume that, of the two competing processes, the emission should have second-order kinetics and that the non-radiative process should be of the first order. In equilibrium, the rate of excitation would be balanced by these two decay processes. This leads to an equation of the form

$$I=B+C(B)^{\frac{1}{2}}. \tag{1}$$

where I is the exciting intensity, B the brightness of the phosphor and C the constant. For large enough B, namely $(B)^{\frac{1}{2}}\gg C$, the first term prevails and we have

$$B=I; \tag{1.1}$$

for small enough B, namely $(B)^{\frac{1}{2}}\ll C$,

$$B=I^2/C^2, \tag{1.2}$$

that is, proportionality with I^2, and a strong dependence upon the coefficient, C. Its physical interpretation leads us to expect that C should be of the form

$$C=aPe^{-E/kT}, \tag{2}$$

containing the concentration, P, of quenching atoms and a Boltzmann factor. Roughly, the condition,

$$(B)^{\frac{1}{2}}=aPe^{-E/kT}, \tag{3}$$

separates not only the ranges of linearity and quadratic dependence but also of temperature independence and temperature quenching; and of insensitiveness to poisoning and reduction of efficiency with the square of the concentration of quenching atoms (which, in our experiments, were mostly nickel). Furthermore, there should be a peculiar dependence of these various factors upon each other, e.g., the tolerance limit for poisoning should be higher at lower temperature, and at higher intensity; and the drop in the temperature-dependence curve of the efficiency should be shifted to lower temperatures by poisoning, or by a reduction of intensity. Qualitatively, all these consequences of (1) and (3) are borne out by the facts.[3] Quantitatively, however, we found appreci-

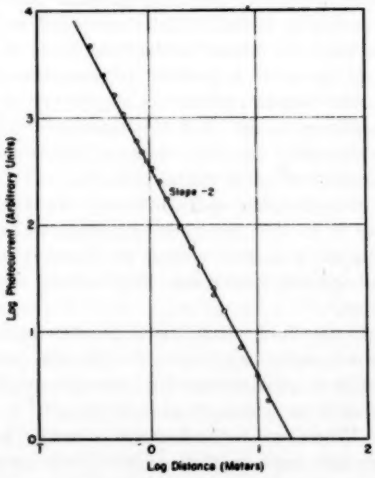


FIG. 1. Check of linearity of measuring system.

* Presented at the Winter Meeting of the Optical Society of America, March 10, 1949 at New York, New York.

† Communication No. 1260 from the Kodak Research Laboratories.

[1] Demonstration by F. Urbach at Winter Meeting of the Optical Society of America, March 7–9, 1946, in Cleveland, Ohio.

[2] D. Pearlman and F. Urbach, J. Opt. Soc. Am. 36, 709 (1946).

[3] N. R. Nail, D. Pearlman, and F. Urbach in *Preparation and Characteristics of Solid Luminescent Materials* (John Wiley and Sons, Inc., New York, 1948), p. 190.

able deviations from these simple equations. The most serious ones were apparently some cases in which the brightness increased more rapidly than with the square of the exciting intensity.

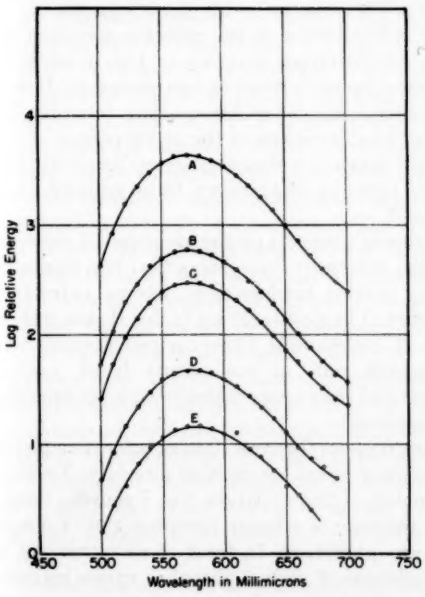
We tried, therefore, to refine the theory by a detailed model of electron transitions between conduction band, filled band, activator levels, and poisoning impurity levels (cf. Appendix). These calculations did not, however, yield a stronger dependence upon intensity than do Eqs. (1) and (2). Neither did the theory developed by Klasens who obtained at first[4] an even weaker dependence upon intensity but derived later[5] our Eq. (1) from a very plausible modification of his treatment, which was based on a model first suggested by Schoen.

In view of the theoretical difficulties involved, we found it desirable to improve and expand our experimental material. In particular, we wanted to determine how large deviations from linearity could be obtained in a carefully prepared well-defined group of phosphors and to measure the very interesting dependence upon poison concentration.

The major requirements for this work were:

1. A series of well-defined preparations with varying poison content.

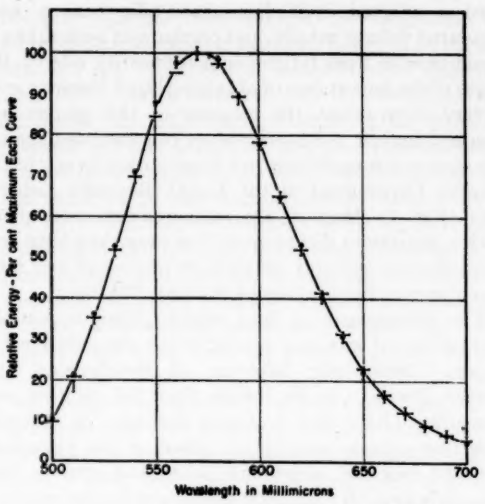
2. A stable exciting source, preferably monochromatic, and variable in a well-defined manner over a large range.



Curve	Rel. Intensity
A	100
B	40
C	31
D	17
E	12

FIG. 2. Independence of emission spectra on exciting intensity for zinc cadmium sulfide, 400 ppm Ag, 4.8 ppm Ni.

[4] H. A. Klasens, Nature **158**, 306 (1946).
[5] M. E. Wise and H. A. Klasens, J. Opt. Soc. Am. **38**, 226 (1948).



Curve	Ni, ppm	Rel. Brightness of Peak
⊙	0.0	100
—	1.0	70
I	4.8	14

FIG. 3. Independence of emission spectra on poison concentration for zinc cadmium sulfide.

3. A stable, linear, measuring system covering a large range, and, particularly, capable of use at very low levels of brightness.

After some preliminary work, we decided to use phosphors with the composition: ZnS 50 percent; CdS 50 percent by weight with 400 ppm of silver as activator; 2 percent sodium chloride as flux; and from 0 to 20 ppm of added nickel. The phosphors were fired at 1090°C for 30 minutes, thoroughly washed in distilled water, and coated with silica, which was shown not to affect our results. Analyses of the completed phosphors showed that no nickel was lost in firing or in subsequent treatment. A practically infinitely thick layer of phosphor was used in all measurements.

For ultraviolet excitation, a high pressure mercury arc was used, operated on direct current, with Corning 5860 and 738 glasses to provide quite pure 365-mμ radiation.

The output of the lamp-filter combination was monitored with a photo-cell whose amplified output was used to control the current through the lamp. This system of stabilization, while fairly complex, was found necessary because fluctuations in the exciting light were multiplied more than three times by the phosphor.

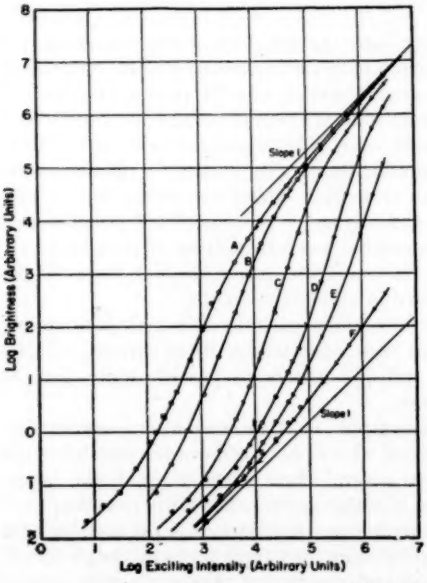
Lamp and monitoring photo-cells were mounted on the carriage of a vertical optical bench. By varying the distance and by using two carefully calibrated neutrals in the practically monochromatic beam, an intensity range of nearly 1:400,000 could be covered. The computed intensities were checked against a barrier-layer cell that was known to have a strictly linear response.

For measuring the light emitted by the phosphor, we

used a selected multiplier photo-tube with a well-regulated voltage supply, and precautions were taken to avoid trouble from fatigue or non-linearity effects. Because of the importance of obtaining strict linearity over a very large range, the response of this system was checked against the barrier-layer cell and also against the square-law variations in a large optical bench in the Physics Department of the Kodak Research Laboratory (Fig. 1). Most of the measurements were made with a potassium dichromate filter over the photo-cell. The effective spectral response of photo-cell and filter was a narrow band centered at about 575-mμ.

The arrangement of light source, phosphor sample, and photo-cell was very similar to the one shown in the paper, "Asymptotic Behavior of Spontaneous and Forced Decay." To be certain that the exciting and measuring filters were mutually exclusive, a diffusely reflecting sample was put in place of the phosphor. Crushed rock salt, aluminum, brass, and several other materials were all too highly fluorescent for use with our extremely sensitive arrangement. The only material which we found suitable for this purpose was sand-blasted platinum. Considerable difficulty was also encountered with the fluorescence of all the optical parts, and even of most black paints which we used to cover them.

The filters and particularly the phosphor samples were kept from being heated during measurement by an air stream.



Curve	Nickel Added	Maximum Slope
A	0 ppm	2.29
B	0.3 ppm	2.68
C	1.0 ppm	3.30
D	3.0 ppm	3.38
E	5.0 ppm	3.06
F	20.0 ppm	1.45

FIG. 4. Dependence of brightness of emission upon exciting intensity for zinc-cadmium sulfide, silver phosphors with different amounts of nickel.

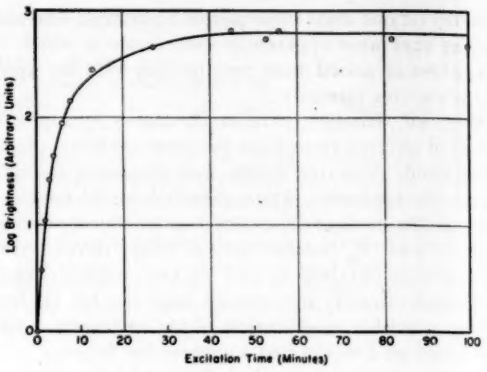


FIG. 5. Build-up of brightness during excitation for zinc cadmium sulfide, 400-ppm Ag.

Since the measurements were made in a fairly narrow spectral range, a shift of the emission spectra upon variation of intensity or of nickel concentration could have distorted dependence of efficiency upon either variable.

Figure 2 shows the emission spectra of a single sample at different levels of excitation. There is no shift of emission. The ordinate in this plot is logarithmic.

The independence of the emission spectrum on the poison concentration is shown in Fig. 3, while Fig. 4 represents the main series of measurements. It is a plot of log brightness *versus* log exciting intensity for six different concentrations of the nickel poison. As can be seen, the maximum slopes range up to about 3.4, and have no pronounced tendency to be grouped around a value of 2.

We should comment on the lower end of these curves. At these extremely low intensities, the slowest components of this luminescence become naturally preponderant. The slow build-up in this region is shown in Fig. 5. If, for example, these components are the short wave-length ends of the copper band, both their slowness and their lower dependence upon intensity are to be expected.

Figure 6 shows the same data as before in a plot of the log efficiency *versus* log exciting intensity. To illustrate the rapidity of this variation, Fig. 7 shows a linear plot of the response of a linear phosphor and of one of the non-linear phosphors. In front of an ultraviolet lamp, the brightness of such a phosphor varies impressively with the inverse seventh power of the distance.

Figure 8, a plot of logarithm of efficiency *versus* nickel concentration for one level of excitation, shows the extremely strong dependence of efficiency upon poisoning. At low poison concentrations, this dependence is approximately exponential. Between 0.5 and 1.5 ppm of added nickel, the efficiency drops by a factor of 75. According to our theoretical equations, it should drop at

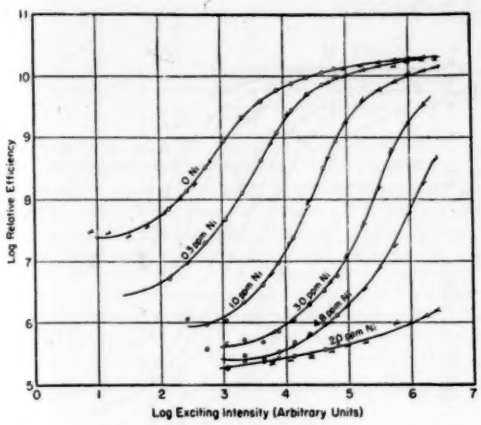


FIG. 6. Dependence of efficiency upon exciting intensity for zinc cadmium sulfide silver phosphors.

most by a factor of 9. This is the more remarkable when it is considered that in the phosphor with 1 ppm of nickel, there is only one atom of poison for about 200 atoms of activator. It is interesting to note that, at low intensities, the effect of nickel is observable with the nickel atoms several hundred lattice distances apart.

Figure 9 represents a set of concentration-dependence curves at different intensity levels on a log-log plot. While the precision of these data is not high, owing to temperature variation, the curves show fairly well the effect of intensity of excitation on the relation between poisoning and efficiency. Curve Y is not part of this set of measurements. It represents the more precise data of Fig. 8, taken at a much later date. The relative intensity for this curve was not available in terms of the arbitrary intensity scale used in the other curves of Fig. 9. It was inserted where it seemed to fit best, with the purpose of showing that the older data, although less precise, give correctly the general shape of the concentration-dependence curves. The curves are much steeper and farther apart than the simple theories would predict.

In the course of this work, attempts were made to determine the effect of absorption, either of the exciting light or of the emitted light, within the thick layer used. We were not able to obtain any clear-cut experimental results. However, it can be shown easily on theoretical grounds that in any region where the log-log plot is a straight line, absorption can have no appreciable effect on its slope.

Confronted with the serious failures of the equations given at the beginning, one may feel compelled to drop the present theories entirely and to look for radically different explanations. We have done so, but the only suggestions of this kind which we can offer—and which we shall discuss elsewhere—do not seem attractive. In view of the fact that our equations describe the general qualitative behavior of the phosphor quite well, modifications of the present theory must be considered.

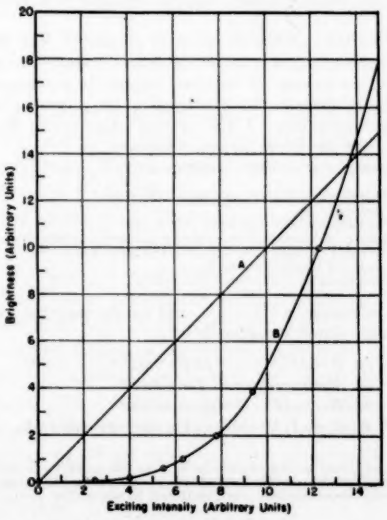
We may combine, for example, the hypothesis of stimulation by the exciting light mentioned in an earlier paper with the hypothesis of competition of different orders. This yields a response with no more than the third power, an unsatisfactory result of an artificial hypothesis. Another possibility that must be considered, as Klasens has already pointed out in a different context, is the influence of slow components or deep traps—whose importance at low intensity levels we have just demonstrated. Our attempts to introduce this effect into the theory have not, thus far, had the desired results.

The most promising approach seemed to be the consideration of saturation phenomena which may very well occur but have been neglected thus far. In the picture which we are using, the poison atoms may not get rid of electrons as quickly as they catch them. This would mean that the effective poison concentration expressed by P in Eq. (2) decreases with increasing brightness. It is easily seen that this is equivalent to a nonluminous process of an order lower than one, and it leads actually to an intensity-dependence stronger than the second power. All these speculations, however, are not satisfactory, and more theoretical study is needed to clarify the situation.

APPENDIX

As mentioned in the text, the model discussed below[a] has not, as yet, yielded more satisfactory results than that of Schoen or Klasens; it is, however, sufficiently different from that model with respect to the role of the poison centers and the possibility of saturation to make it potentially valuable.

Schoen and Klasens assume that the poison centers act like activator centers. They can accept an electron after having lost



A—Linear Phosphor
B—Superlinear Phosphor—(3.0 ppm Ni of Fig. 6)

FIG. 7. Comparison of linear and superlinear phosphors.

[a] Cornell conference on luminescent materials in October 1946 (John Wiley & Sons, Inc., New York, 1948).

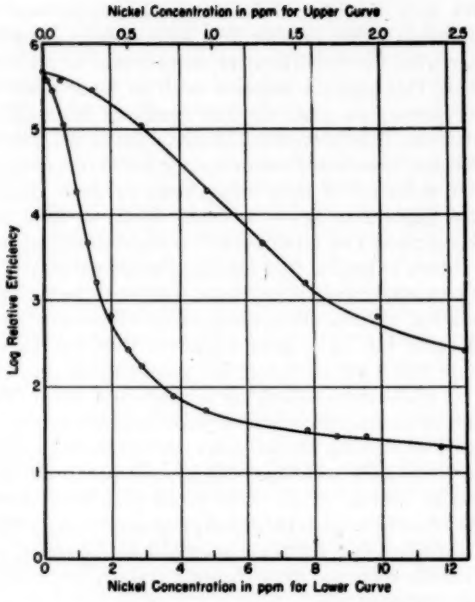


FIG. 8. Effect of poisoning on efficiency of zinc cadmium sulfide.

one by excitation. We assumed, on the contrary, that the poison centers act like traps, capturing electrons in their normal state.[b] In order to remain effective, they must lose these electrons in a non-radiative process, which, however, must in the end replace the electron in the activator hole. This leads to the assumption that hole-migration participates in the non-radiative part of the process. Several variants of this scheme have been considered. A brief discussion of one example follows; no details are given because of the formal analogy with the schemes of Klasens and of Schoen.

Let N be the number of activator centers; P, the number of poison centers; y, the number of holes "trapped" in activator centers; x, the number of electrons trapped in poison centers; h, the number of holes in the filled band; n, the number of electrons in the conduction band; I, the exciting intensity; B, the emitted intensity; and the Greek letters, constants.

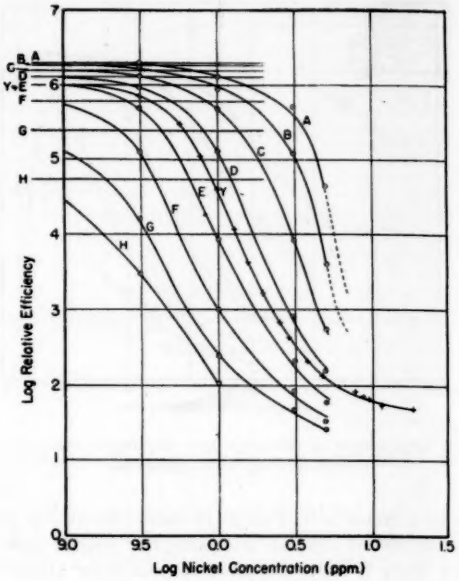
The rates of the various processes are:

Direct excitation of activator centers: $\alpha J(N-y)=I$.
Emission: $\beta ny=B$.
Electron trapping by poison atoms: $\gamma n(P-x)$.
Thermal release of electrons from poison atoms to conduction band: κx.
Trapped electrons recombining with holes in filled band: ϵhx.
Thermal release of trapped holes: ∂y.
Hole-trapping by activator atoms: $\pi(N-y)h$.

We have, of course, $n+y=h+x$, and for the stationary condition in the four states considered:

$$dn/dt=\alpha J(N-y)-\beta ny-\gamma n(P-x)+\kappa x=0.$$
$$dh/dt=\partial y-\epsilon hx-\pi(N-y)h=0.$$
$$dx/dt=\gamma n(P-x)-\epsilon hx-\kappa x=0.$$
$$dy/dt=\alpha J(N-y)+\pi(N-y)h-\partial y-\beta ny=0.$$

[b] As the auxiliary activator centers in infra-red-sensitive phosphors seem to do. One advantage of this assumption in explaining the strong influence of low poison concentrations was mentioned in our earlier discussion of the subject.



Exciting Intensities

A—25,000	E—250
B— 8000	F— 80
C— 2500	G— 25
D— 800	H— 8

Y—Unknown

FIG. 9. Dependence of efficiency upon concentration of poison for various values of exciting intensity.

These equations lead to an equation of the sixth order. Let us consider as an example of a special case the conditions:

$$N\gg y, \quad \text{(a)}$$
$$P\gg x, \quad \text{(b)}$$

characterizing a state of excitation far from saturation, and the following set of assumptions concerning the various constants:

$$\pi N\gg\partial, \quad \text{(c)}$$
$$\gamma P\gg\kappa, \quad \text{(d)}$$
$$\gamma P\gg\partial. \quad \text{(e)}$$

Using these assumptions, we obtain after some calculation,

$$I=B+(\gamma/\beta)\partial P(B)^{\frac{1}{2}}.$$

This is of the form of Eq. (1) in the text; referring to the measuring of the constants, we see immediately that the factor of $(B)^{\frac{1}{2}}$ is of the general form of C in that equation. Of course, the above set of inequalities is not the only case which yields this result. Another such set is:

$$N\gg y, \quad P\gg x, \quad \partial\gg\pi N, \quad \gamma P\gg\kappa, \quad \gamma P\gg\pi N.$$

No great importance need be attached to either set. They serve only to illustrate the compatability of the model expressed in the above set of equations with Eq. (1). Dropping either or both of the conditions, $N\gg y$ and $P\gg x$, does not seem to yield a stronger than quadratic intensity-dependence in such cases as we were able to survey.

Simplified Lenard Phosphors*,†

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(Received May 2, 1949)

Attempts were made to obtain well-defined and simple singly activated strontium sulfide phosphors. This paper is concerned with the effect of strontium oxide, an unavoidable constituent of strontium sulfide phosphors, on copper- or bismuth-activated strontium sulfide phosphors with strontium chloride as flux. Two different phenomena are encountered with variation in concentration of strontium oxide. One, observed with both copper and bismuth activation, is a gradual shift in emission. The other, obtained with bismuth-activated phosphors, is a surprisingly abrupt change of the emission band. In each case the effect of various oxide concentrations was found to depend upon the concentration of the strontium chloride flux. The distribution coefficient of the activators between strontium sulfide and strontium oxide, the solubility of strontium oxide in strontium chloride, and other solubility relationships largely determine the changes in the emission characteristics.

In the continued search for simple luminescent systems, the investigation was extended to strontium oxide phosphors. Anionic impurities and flux can be avoided and at least some of these phosphors exhibit the essential characteristics of the complex Lenard phosphors. Copper was found to act as an activator only if present in the univalent state.

THE early literature[1] on Lenard phosphors contains complicated and often unreliable directions for their preparation. Recently, attempts have been made, with increasing success, to replace these empirical methods by simpler and more understandable methods of preparation. In some instances, the influence of certain ingredients has been investigated systematically, and has revealed unexpected complexities which must be partly responsible for the inconsistency and disorder in the early literature. It has been found that the independent action of activators in multi-activated alkaline earth sulfide phosphors is the exception rather than the rule;[2–4] that the sensitivity of the luminescent systems to small traces of cationic impurities is even greater and more complex than was suspected heretofore;[5] and that some components, formerly regarded as inert fillers,[3,6,7] are of critical importance for many phosphors. The presence of sulfate ion has been shown to aid in the fluxing of certain phosphors, and the presence of small amounts of oxide[8,9] has been found to exert considerable influence on stimulability.

In the present paper the authors describe an attempt to prepare synthetically well-defined and constitutionally simple phosphors of the Lenard type. Strontium sulfide was used as the base and copper or bismuth was used as the single activator. Because copper is most difficult to avoid as a contaminant of most phosphors, it was selected to ensure the presence of but one activator in the phosphor. Bismuth was chosen because it is a very effective activator of the alkaline earth sulfide class, while strontium chloride was used as a flux since it would introduce but one other ion into the system.

From our experience with doubly activated infra-red-sensitive phosphors[9] and from the work of Ward and others,[8,9] we know that strontium oxide affects the stimulability of these phosphors. Stripp and Ward[9] have also shown that it is not possible to synthesize strontium sulfide free from strontium oxide with present methods and that the amount of oxide, produced by a side reaction, varies from batch to batch. Therefore, the decision was made to investigate first the effect of the addition of small amounts of strontium oxide to the phosphors.

The phosphors were prepared by the technique used recently[8,9] for the doubly activated infra-red-sensitive phosphors. The emission spectra were obtained by means of a double monochromator and selected multiplier photo-cells. The arrangement was calibrated against a standard lamp of known color temperature.

Figure 1 shows the fluorescence spectra of a number of copper-activated strontium sulfide phosphors. They were prepared with 6 percent strontium chloride flux and 100-ppm activator, and they differ from each other only by the amount of strontium oxide deliberately introduced. The emission spectrum shifts from deep blue to green as the oxide content is increased. The first few percent of added oxide causes a pronounced shift in the emission, while the effect of further increase of oxide is less marked.

Close inspection of the curves indicates the appearance of new bands or humps whose gradual change in intensity may very well cause the shift in the spectrum. In the doubly activated infra-red-sensitive phosphors, a

* Presented at the Winter Meeting of the Optical Society of America, March 11, 1949 at New York, New York.

† Communication No. 1258 from the Kodak Research Laboratories.

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[6] F. A. Kroeger and J. E. Hellingman, J. Electrochem. Soc. **93**, 165 (1948).

[7] Primak, Osterheld, and Ward, J. Am. Chem. Soc. **69**, 1283 (1947).

[8] Smith, Rosenstein, and Ward, J. Am. Chem. Soc. **69**, 1725 (1947).

[9] K. F. Stripp and R. Ward, J. Am. Chem. Soc. **70**, 401 (1948).

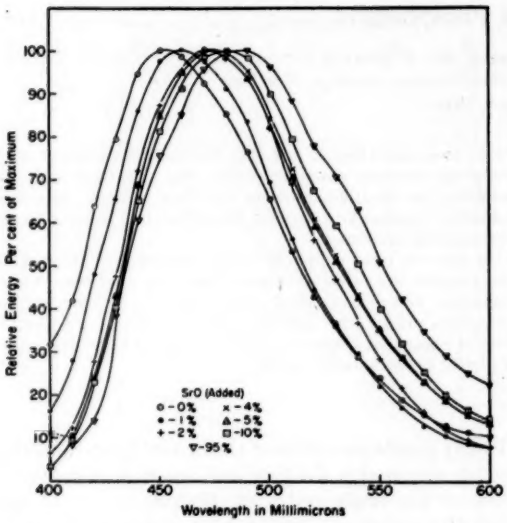

FIG. 1. Dependence of emission spectrum of copper-activated strontium sulfide phosphors upon amount of added strontium oxide. 100 parts SrS, 6 percent $SrCl_2$, 100 ppm-Cu, x percent SrO. Phosphor fired in oxygen-free dry nitrogen at 950°C for 30 minutes, then cooled under nitrogen.

trace of strontium oxide enhances the stimulability of the phosphor;[8,9] above that, the stimulability decreases with increasing oxide content. No attempt has yet been made to ascertain the effect upon stimulability of traces of strontium oxide in the copper-activated sulfide phosphors. However, the phosphors containing little or no added oxide are stimulable and the stimulability decreases with increasing oxide content. Thermoluminescence is present in all cases.

Figure 2 shows the fluorescence spectra for a set of bismuth-activated strontium sulfide phosphors containing 12 percent strontium chloride flux and 100-ppm bismuth. Again, the phosphors differ from one another by the amount of added strontium oxide. As the oxide is increased, the long wave-length end of the band is raised. Then at a certain oxide concentration, the band disappears abruptly and a new band appears in the blue. Thus, two distinctly different phenomena are present, both brought about by the increasing concentration of strontium oxide. One is a gradual change, very similar to the gradual change observed in the shift of the copper band. The other is a surprisingly abrupt shift of the emission band.

The oxide concentration at which the one band disappears and the other appears occurs in this set of samples between 3–4 percent. It was found, however, that the oxide concentration which causes this shift varies with the concentration of flux. At 6 percent flux, the break occurs at about 1–2 percent added oxide, and at 3 percent flux concentration, it occurs at about 0.5–1 percent added oxide. In each case, these figures correspond to the limit of solubility of strontium oxide in strontium chloride at the temperature of firing of the phosphor. However, at room temperatures, there seems to be no strong intersolubility of any of the solid constituents. X-ray analysis of these phosphors shows a number of thus far unidentified weak lines. At the most, only very small amounts of new phases can be present. This is essentially in agreement with the findings of Primak.[10]

As in the case of the copper-activated phosphors, the bismuth phosphors which contain little or no added oxide are stimulable and the stimulability decreases with increasing content of strontium oxide. Here, too, all the preparations show thermoluminescence.

To return for a moment to the question of change in emission spectra with change in flux-oxide ratio, the oxide-produced shift in emission of the copper-activated series also depends upon the amount of flux present. Increase in flux concentration requires an increase in the amount of oxide added in order to bring about a given spectral shift. Similarly, an increase in flux concentration also requires an increase in the amount of added oxide in order to bring about a drop in stimulability of both the copper-activated and bismuth-activated phosphors. This phenomenon has also been observed with doubly activated infra-red-sensitive phosphors: Phosphors which have little or no infra-red-sensitivity due to too high an oxide content can be made infra-red-sensitive by the addition of more flux. Thus, the effect of the flux in suppressing or decreasing the effect of the addition of oxide seems to be a quite general phenomenon. Some additional observations and data taken from the literature on the solubility of the strontium salts involved help in understanding the phenomena thus far discussed, particularly with reference to the

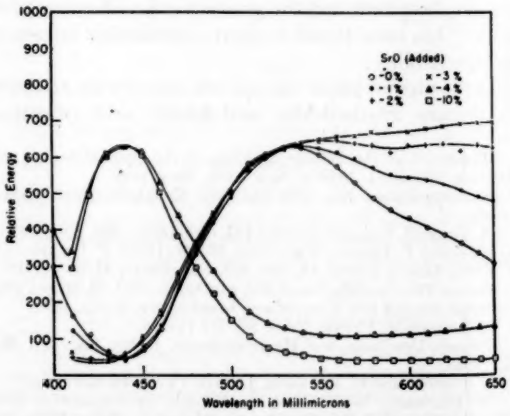

FIG. 2. Dependence of emission spectrum of bismuth-activated strontium sulfide phosphor upon amount of added strontium oxide. 100 parts SrS, 12 percent $SrCl_2$, 100 ppm-Bi, × percent SrO. Phosphor fired in oxygen-free dry nitrogen at 950°C for 30 minutes, then cooled under nitrogen.

[10] Primak, Kaufmann, and Ward, J. Am. Chem. Soc. **20**, 2043 (1948).

sudden shift in the emission spectra of the bismuth-activated phosphor.

At the temperature of firing, strontium chloride is molten. The remainder of the system consists of strontium sulfide, which is soluble in strontium chloride to the extent of about 3 percent, and strontium oxide, which is soluble to about 30 percent in strontium chloride.[11] There is little or no intersolubility between strontium oxide and strontium sulfide. We do not yet know how the solubility relationship of any pair of these components is affected by the presence of the third constituent. However, at the temperature encountered during the preparation of these phosphors, at least two solid phases are present: one consisting essentially of strontium oxide, and the other essentially of strontium sulfide; and one liquid phase which consists principally of strontium chloride. Ward[11] has shown that the activator distributes itself between the flux and the strontium sulfide base, and that the magnitude of this distribution coefficient depends upon the activator and the flux. The presence of strontium oxide also alters the distribution ratio.

Furthermore, it was not possible to prepare a strontium chloride-bismuth phosphor with visible emission. In a strontium chloride-strontium oxide mixture, luminescent samples were obtained only if strontium oxide was present in excess of its solubility in strontium chloride. This luminescence is identical with the blue strontium sulfide-strontium oxide band (Fig. 3).

Let us now consider again the bismuth-activated strontium sulfide-strontium chloride phosphors. The

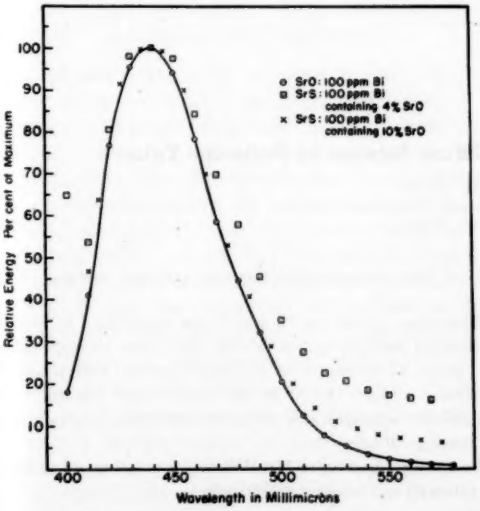
Relative Energy Per cent of Maximum
Wavelength in Millimicrons
o SrO: 100 ppm Bi
□ SrS: 100 ppm Bi containing 4% SrO
× SrS: 100 ppm Bi containing 10% SrO

FIG. 3. Emission spectrum of bismuth-activated strontium oxide phosphor. Points ⊡ and × are taken from Fig. 2. Phosphor fired in oxygen-free dry nitrogen at 950°C for 30 minutes, then cooled under nitrogen.

[11] R. Ward, J. Electrochem. Soc. **93**, 171 (1948). Mason, Hiskey, and Ward, J. Am. Chem. Soc. **71**, 509 (1949).

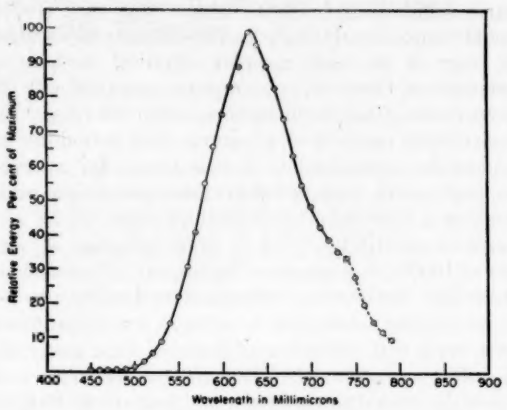

FIG. 4. Emission spectrum of copper-activated strontium oxide; 100 parts SrO, 100 ppm-Cu. Phosphor fired in oxygen-free dry nitrogen at 950°C for 30 minutes, then cooled under nitrogen.

luminescent component of the phosphor with no added oxide is undoubtedly the strontium sulfide phase. In the phosphor containing strontium oxide, we may conclude that the luminescence is due to the strontium sulfide only as long as there is no solid phase of strontium oxide present at the temperature of firing. In the presence of the solid phase of strontium oxide at the temperature of firing, even in very small amounts, the luminescent band is due to strontium oxide. Although the distribution of activator was not determined, it seems evident that the partition is greatly in favor of the strontium oxide.

We must return to the gradual changes with oxide concentration observed in both the bismuth and copper phosphors. These changes are not of the same nature as the distribution changes just discussed. The gradual shift may be due to a distorting effect of the strontium oxide on the strontium sulfide lattice, or perhaps to a gradual formation of another phase, too weak to be clearly shown by the x-ray analysis.

In the case of copper, the distribution of activator between the phases is apparently different from the case of bismuth. It seems that the copper is far more soluble in strontium sulfide than in strontium oxide, for the oxide band does not appear even in the phosphor containing 95 percent strontium oxide. The phenomenon of gradual shift of the emission band from blue to green is very likely similar in origin to that of the shift of the long wave-length band of the strontium sulfide-oxide-chloride bismuth system.

It is apparent, therefore, that the strontium oxide influences the luminescence spectra of sulfide phosphors in two different ways. One of these may be due either to distortion of the sulfide lattice or to the formation of a completely new phase. The other is brought about by the solubility relationships of all the constituents of the luminescent system.

The type of problem dealt with in this investigation is likely to be encountered in any detailed study of alkaline-

earth sulfide phosphors. We believe that such studies could comparatively easily lead to complete clarification of some of the more complex empirical methods of preparation. However, we were more concerned with the preparation of simpler phosphors, and in this respect the unavoidable presence of strontium oxide introduces an undesirable complication. In our search for an even simpler system, we were led to examine strontium oxide itself as a base material. Strontium oxide can be prepared in quantitative yield by firing strontium carbonate at 1000°C in a stream of hydrogen.[10] (Inasmuch as strontium carbonate or strontium hydroxide may be formed during subsequent handling, a few preparations were made with deliberate additions of these materials. No effect was observed.) The activators as oxides were mixed dry with strontium oxide and fired at 950–1000°C. No flux was required and hence we have apparently a simple luminescent system. The bismuth-activated strontium oxide phosphor can be prepared in a neutral or oxidizing atmosphere. A reducing atmosphere yields a non-luminescent preparation which is gray in daylight. This grayness is probably due to metallic bismuth.

Figure 3 shows the fluorescence spectrum of a strontium oxide phosphor containing 100-ppm bismuth. It is identical with both the short wave-length band of the strontium sulfide phosphor which contains sufficient amounts of strontium oxide and the band produced by the fluorescent strontium oxide-strontium chloride mixture. The bismuth activated strontium oxide phosphors show little afterglow at room temperature, but they do have traps. as evidenced by appreciable stimulation and distinct thermoluminescence.

The fluorescence spectrum of a copper-activated strontium oxide phosphor appears in Fig. 4. The phosphor can be prepared from either the cupric or cuprous oxide by firing in an inert atmosphere. Above 900°, the thermal decomposition of cupric compounds to cuprous is appreciable.[12] Hence, at the temperature of preparation, the activator should be in the cuprous state. If the preparation is cooled in a neutral atmosphere, it is luminescent, while if it is cooled in air or oxygen, it is not. Thus, we conclude from these facts that the copper activator is in the univalent state. The copper-activated strontium oxide phosphor, like the bismuth phosphor, also shows weak afterglow, distinct stimulability, and strong thermoluminescence.

Flux-free strontium oxide phosphors appear to be systems of simple constitution and are easily prepared. Unfortunately, it seems to be very difficult to prepare the phosphors as large single crystals. Nevertheless, if further work should show that the simplicity of constitution is accompanied by a simpler than usual behavior, this material should be quite valuable for fundamental research.

[12] W. M. Lattimer and J. H. Hildebrand, *Reference Book of Inorganic Chemistry* (The Macmillan Company, New York, 1946), p. 106.

Addendum: Transmission of Light from Diffuse Sources by Periscope Tubes

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Research Laboratory, General Electric Company, Schenectady, New York
[J. Opt. Soc. Am. **39**, 393 (1949)]

SINCE our article appeared, it has been pointed out by Mr. J. E. Wilkins, Jr., of the American Optical Company that the integrals V_1 and V_2 appearing in Eq. (30) are integrable by analytic means, and that our statement that "they are not integrable by analytical methods" is indeed false.

The values given by Wilkins for these integrals are

$$V_1=\int_{1-\gamma}^{1+\gamma} z\sin^{-1}\left(\frac{z^2+1-\gamma^2}{2z}\right)dz=\pi\gamma\left(1-\frac{\gamma}{2}\right),$$

$$V_2=\int_{1-\gamma}^{1+\gamma} z\sin^{-1}\left(\frac{z^2-1+\gamma^2}{2\gamma z}\right)dz=\frac{\pi\gamma^2}{2},$$

and we have since verified them by our own analytic integrations.

When these values for V_1 and V_2 are substituted in Eq. (29), the bracket multiplying the $(\pi^2a^4B)/(4F^2)$ term becomes identically unity, independent of γ, which proves analytically the conclusion already drawn in the article that the total light transmission is independent of the position of the light source over the range $\gamma=0$ to $\gamma=1$.

We are very grateful to Mr. Wilkins for pointing out to us that the integrals can be done analytically.

Temperature-Dependent Structure of the Emission Spectra of Two Crystalline Forms of the Zinc Silicate: Mn Phosphor

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(Received May 2, 1949)

The emission-spectra (excited by short ultraviolet) of two crystalline forms of the zinc-silicate:Mn phosphor have been recorded photographically. A number of operating temperatures were used. The rhombohedral form, normally green-emitting, develops a yellow band at elevated temperatures. The high-temperature-quenched form, normally yellow-emitting, develops two green bands at lowered operating temperatures. Analysis indicates the possibility that the same bands are potentially present in both forms, but the effect of the different configurations is to emphasize different bands, especially with regard to their response to changes in temperature of operation. In addition to the "band" structure, "fine" structure was found for both forms at the lowest operating temperature (−196°C).

THE efficient and commercially important Zn_2SiO_4:Mn (0.3) phosphor has heretofore been studied chiefly in its stable rhombohedral (α) crystal form. There is another crystalline modification of zinc silicate, formed by rapid quenching from a melt, which also forms an efficient phosphor when made with about 0.3-weight percent of manganese activator.[1,2]

Through the use of the photographic method in conjunction with a grating spectrograph, and by using temperatures of operation ranging from −196°C to 400°C, this second, or β-form, is here shown to have complex spectra which have not yet been reported in the literature. Under the same conditions, details in the spectra of α-Zn_2SiO_4:Mn have been observed which also have escaped prior notice. A comparison between the spectra of the α- and β-forms indicates a close correlation between their component bands.

EXPERIMENTAL METHODS

The present data were obtained by recording the various emission spectra on panchromatic film. A grating spectrograph was used in the conventional Rowland arrangement. Resolutions ranging from 1A to 15A were used. The density-exposure characteristic of the film was determined for each emulsion used for recording the spectra, but the exact nature of the spectral-sensitivity of the film was not determined at this stage. Spectral distributions shown herein (Fig. 1 and Fig. 2) must be considered only as first approximations to the true distribution. A very simple type of "oven-refrigerator" was designed whereby a thin disk of phosphor with an imbedded thermocouple could be chilled to liquid-nitrogen temperature or raised to +400°C. A double-window of Corning 791 glass was used for both excitant ingress and emission egress. The excitant was chiefly strong 2537A emission from a low pressure mercury arc as transmitted by a Corning 9863 filter. Measurements were made on the excited side of very thick coatings of the phosphor samples having average particle sizes of the order of one micron.[3]

RESULTS

Originally this investigation was intended only to resolve some disagreement in the literature[4,5] as to the effect of low temperature operation on the peak wave-length of α-Zn_2SiO_4:Mn. Since some of the perturbing effects of high activator concentration have been known for some time,[2] the value for activator-concentration of 0.3 percent by weight of manganese was selected as a compromise. The superimposed densitometer records in Fig. 3a are typical, and show conclusively the shift, by 50A, of the apparent peak wave-length between the two temperatures of operation, 25°C and −196°C. Other records, not reproduced, show that most of the shift occurs near the low temperature end of the range. Test exposures with incandescent sources show the film to have no vagaries in its characteristics sufficient to account for these results. Attention is called to the sharp cut-off on the short wave-length side of the

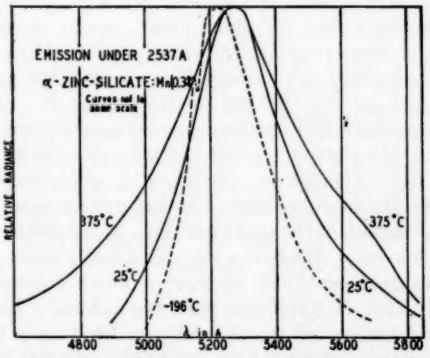

FIG. 1. Spectral distribution of the photoluminescence-emission-spectrum of α-zinc silicate:Mn at three operating temperatures.

[1] A. Schleede and A. Gruhl, Zeits. f. Elektrochemie u. angewandte physik. Chem. **27**, 411 (1923).
[2] H. W. Leverenz and F. Seitz, J. App. Phys. **10**, 479 (1939).
[3] H. W. Leverenz, Science **109**, 183 (1949).
[4] F. J. Studer and Louise Gaus, *Cornell Symposium on Solid Luminescent Materials* (John Wiley and Sons Inc., New York, 1948).
[5] E. A. Ab, Bull. Acad. Sci. SSSR **9**, 467 (1945).

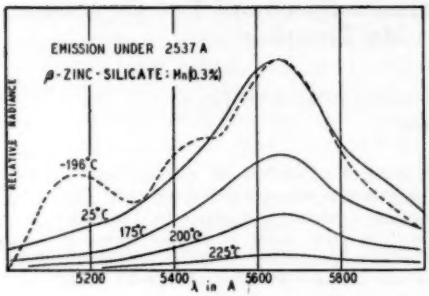

FIG. 2. Spectral distribution of the photoluminescence-emission-spectrum of β-zinc silicate: Mn at five operating temperatures.

spectra obtained at low temperature, and to the considerable asymmetry of the band. The suggestion is strong that there exist at least two bands: one narrow band at 5225A with a large negative temperature-coefficient (decreasing efficiency with increasing temperature) near −196°C, and one broader one at 5275A with a positive coefficient.

In addition to this finding, two other unexpected results were obtained. One is seen in the densitometer record reproduced in Fig. 3b. At 5155A a sharp "line" is found in the emission-spectrum of α-Zn_2SiO_4: Mn operated at −196°C. A less pronounced indication of this line may be seen in the record in Fig. 3a. Four samples of α-zinc silicate: Mn, made under various conditions and from different raw materials, were all found to emit this line. The second unexpected result was the appearance of a yellow band at about 5700A when the α-zinc silicate: Mn was operated at elevated temperatures. This is shown in Fig. 1, where film densities have been converted to approximate relative-radiance values.

An emission band near 5700A has previously been reported when a special method of preparation was used. Fonda[6] found that heating a mixture of zinc, silicon, and manganese oxides for short times, would produce a material whose emission was yellow in color. The author and co-workers have shown that excess silica or zinc oxide are not required for the production of a yellow band in the cathodoluminescence emission from a zinc-silicate: Mn phosphor formed at low crystallizing temperatures.[7] The β-form, produced by quenching zinc-silicate: Mn from the melt, also has its emission in the yellow portion of the spectrum. This β-zinc silicate: Mn phosphor has a different x-ray diffraction pattern.[1,2,7,8] It also has been found to have a lower density and lower index of refraction than the α-form. (The refractive indices of the α-form are 1.694 and 1.723, whereas those of the β-form are 1.685 and 1.695.)*

As with the α-form, its emission-spectrum was photographed at various temperatures of operation. A typical set of densitometer records is reproduced in Fig. 4. Clearly, there are at least four components in the emission-spectrum of β-zinc silicate: Mn. Discernible in the original negative of the spectrum obtained at −196°C, but not reproduced by the densitometer, are two "lines" at 5350A and 5380A. Excitation at elevated temperatures results in the spectral distributions shown in Fig. 2, together with the replotted data of Fig. 4.

The change with temperature of the intensity at the apparent peak wave-length can be described as follows: for the α-form the peak-intensity decreases almost uniformly over the range of temperature covered, having relative values of 1.5, 1.0 and 0.3 at −196°, 25° and 375°C respectively; the peak of the emission for the β-form undergoes little change as the temperature varies from −196°C to about 150°C at which point the decrease in efficiency becomes pronounced with further increase in temperature.

A comparative representation of the structure of the spectra of the two forms of zinc silicate: Mn is given in Fig. 5 where the peak-intensity position of the various possible, or probable, bands and "lines" have been tentatively located on a wave-length scale. An attempt has also been made to indicate the variation (with temperature) of the relative importance of the contribution of each band (or "line") to the spectrum as a whole. The indication of a band at 6000A for the α-form is only tentative, being based on very slight evidence.

DISCUSSION

In his analysis of the spectra of the α-form of Zn_2SiO_4: Mn by the method of fitting Gaussian error curves, Nagy[9] reports bands at 5270A, 5480A, 5710A and 6050A. Butler[10] using the same method, reports that

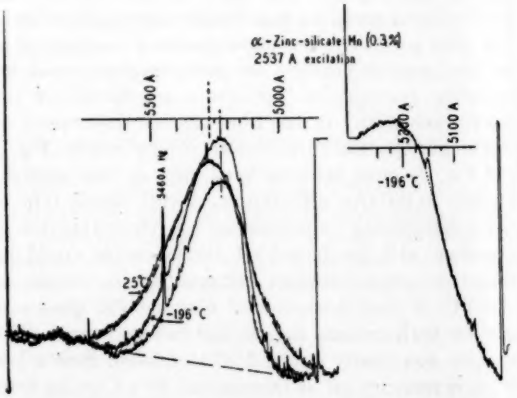

FIG. 3. Densitometer records showing (a) shift of peak wave-length, and (b) presence of a "line" in the photoluminescence-emission-spectrum of α-zinc silicate: Mn obtained at −196°C.

[6] G. R. Fonda, J. Chem. Phys. 44, 851 (1940).
[7] A discussion of this and related data will appear in a book now in press: H. W. Leverenz, *Introduction to Luminescence of Solids* (John Wiley and Sons Inc.).
[8] H. P. Rooksby and A. H. McKeag, Trans. Faraday Soc. 37, 308 (1941).
* Measurements by J. Gallup, Radio Corporation of America, Victor Div., Harrison, New Jersey.
[9] Elemer Nagy, J. Opt. Soc. Am. 39, 42 (1949).
[10] Keith H. Butler, J. Electrochem. Soc. 93, 143 (1948).

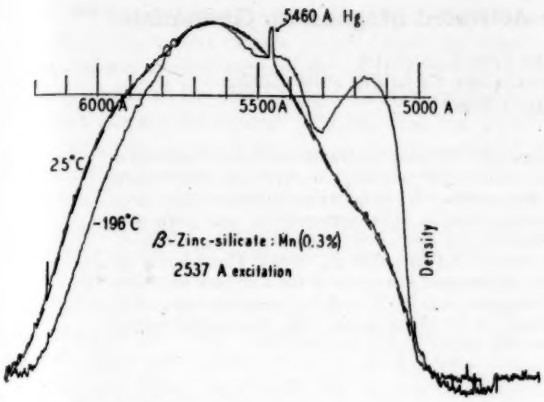

FIG. 4. Densitometer records of the photoluminescence-emission-spectrum of β-zinc silicate: Mn at two operating temperatures.

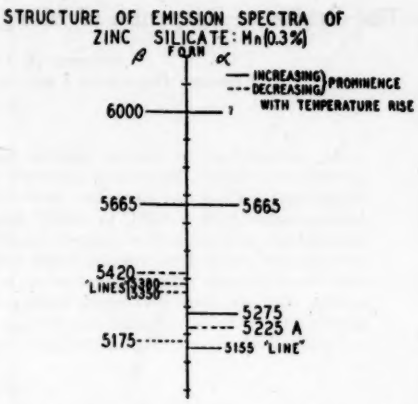

FIG. 5. Schematic of the spectral complex of the photoluminescence of two crystalline forms of zinc silicate: Mn. Lines represent the position of peak-wave lengths of the emission bands and "lines."

components at 5250A, 5460A, 5780A and 6100A may account for the structure of the spectra for all of his various samples of zinc-beryllium silicate activated with manganese. In both analyses, the band near 5470A was not detected directly but established as a "remainder" when the more definite bands had been subtracted. It is to be noted that there is a difference of approximately 250A (0.11 ev) between the two green bands (5175A, 5420A) of the β-form at −196°C, and also between the 5225A band (reported by this paper for the α-form at −196°C) and the band at 5470A (averaged) reported by both Nagy and Butler for the α-form. Making the assumption that the 5175-A band of the β-form is related to the 5225-A band of the α-form, it would seem that the definite existence of a 5420-A band for the β-form may independently justify their assumption of the existence of a 5460 to 5480A band. Nagy's disagreement with Butler as to the characteristics of a 5250A band may possibly be explained by his failure to detect the further complexity of the structure within the range 5225A and 5275A. Further, though the samples used in this investigation apparently are a close match for sample *B* of Nagy, the spectrum from the α-form at liquid-nitrogen temperature had no appreciable intensity at 5000A, whereas Nagy reports an intensity amounting to 20 percent of peak-intensity.

During discussion of these data with H. W. Leverenz, the following tentative interpretation was evolved:[7] From the information available on the properties of the α- and β-forms of the zinc silicate: Mn(0.3) phosphors, it appears that the Mn activator atoms (ions to some variable degree) are in substitutional sites in both forms. In both the α-(rhombohedral) and β-(probably hexagonal or tetragonal) forms, therefore, the Mn activator atoms are apparently surrounded by four tetrahedrally arranged oxygen atoms which effectively shield the central Mn atom from the first-order effects of change in structure of the host crystal. The observed emission lines are undoubtedly occasioned by transitions involving redistributions of electrons in the inner unfilled 3*d* states of Mn. The appearance of several component bands common to both the α- and β-forms (Fig. 5) indicates that the energy levels of the 3*d* and 4*s* electrons of the Mn activator atoms are near each other, or that the 3*d* and 4*s* states are to some degree hybridized in bonding with the 2*p* states of the surrounding oxygen atoms. The different relative intensities of the component bands observed with change in crystal structure and temperature are interpreted as being caused by (1) changes in the relative energy-level heights and electron distributions in chiefly the 3*d* and 4*s* states of the Mn activator atoms and (2) selective enhancement of transition probabilities involving electrons in these levels. The selective effects arise from changes in the magnitude and symmetry of the force fields involved in the structural "contest" between a Mn activator atom (impurity) and its host-crystal environment.

The Emission Spectrum of Manganese-Activated Magnesium Germanate* **

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(Received May 2, 1949)

An unusual fine structure of emission has been reported[1] for some manganese-activated magnesium germanate phosphors. In order to determine the precise nature of the transitions involved, the temperature dependence of the actual intensities, half-widths and peak positions of the individual emission bands have been measured from −190°C to +90°C using ultraviolet excitation. The measurements were made in a constant temperature vacuum sample chamber and with a Littrow type spectrograph containing calibrated photographic plates. Five emission bands were clearly resolved between 6200 and 6800A. The intensity of each band increases with temperature up to a critical temperature above which the efficiency decreases rapidly. Also, the short wave-length bands practically disappear at −190°C, and the individual bands shift slightly to shorter wave-lengths and decrease in half-width at low temperatures. The experimental results are qualitatively interpreted, and tentative correlations with atomic spectra are proposed.

INTRODUCTION

IN a previous publication, Williams[1] has described the emission spectra of some manganese-activated magnesium germanate phosphors. These materials are unique in that they exhibit an unusual fine structure of emission that is peculiar to no other manganese-activated phosphor. The data obtained from the temperature dependence of the actual intensities, half-widths and peak positions of the individual bands of the emission spectrum are useful in accounting for the actual transitions taking place in the crystal lattice and may eventually lend itself to the formulation of a general theory of the mechanism of luminescence of manganese-activated phosphors.

GENERAL DESCRIPTION OF THE APPARATUS

In order to investigate the changes in the emission spectra while subjecting the phosphor to widely separated limits of temperature, it was necessary to construct a special sample holder. The apparatus used for this is depicted in Fig. 1. The sample is placed in a circular recess located on the lower side of the brass plate which is mounted at an angle of forty-five degrees with respect to the spectrograph slits and which is fitted with a thermo-couple for temperature measurement. Two concentric brass tubes, whose annular space is packed with cork, are attached to the top of the sample plate serving as a container for the heating or cooling medium. The sample is enclosed in a vacuum chamber to eliminate water condensation and to permit electron excitation. Two quartz windows are provided in the sample chamber: one for excitation of the phosphor by means of a 500-watt Uviarc ultraviolet lamp and the other to permit the light emitted from the phosphor to reach the spectrograph slits. The ultraviolet light is filtered through Corning No. 9863 before reaching the sample. A Bausch and Lomb spectrograph of the Littrow type is used for recording the spectra photographically. The sample chamber is mounted in such a way that the window which passes the emitted light is as close as possible to the spectrograph slits since the emission intensities are comparatively small.

PROCEDURE

The method employed in the following procedure for the presentation of the spectral data has a decisive advantage over previous methods in that actual intensities of emission are obtained in place of plate densities. In order to obtain intensities, the photographic plates are calibrated to determine the relationship between plate densities and actual emission intensities. The reciprocity principle, which states that light of twice the intensity falling on a photographic plate for one-half the time will impart equal plate densities, allows such a relationship to be made. Calibration is carried out at room temperature by taking a series of exposures of the emission spectrum with varying exposure times and a constant slit width or, conversely, by varying the slit widths and allowing the time factor to remain constant. By using a densitometer, the exposures thus made are plotted as plate densities *versus* distances along the photographic plate. Such a series of plots will be *similar* in appearance to those shown in Fig. 4, but it must be borne in mind that this figure shows the spectra *after* the conversion from plate densities to actual intensities has been made. The preparation of the calibration curve is accomplished by selecting the plate density corresponding to the highest peak on the densitometer plot and assigning to this density some arbitrarily chosen value of emission intensity, e.g., a value of 100. Next a peak is selected, where from the reciprocity principle it is known that the actual light intensity is only one-half that of the former value (a value of 50), and from the same densitometer plot the corresponding plate density is read.

Working the densitometer curves over in this manner yields sufficient data to construct a calibration curve relating actual intensities to the plate densities. Figure 2

* Supported by the ONR through Contract N7onr-284 T.O. 1.
** Presented at the New York meeting of the Optical Society of America, March 10, 1949.
[1] F. E. Williams, J. Opt. Soc. Am. 37, 302 (1947).

illustrates a calibration curve of this type. The conformity of the points which are obtained for two procedures, one using a constant slit width with various time exposures and the other using a constant exposure time with various slit widths, indicates that the reciprocity principle is obeyed for the particular portion of the density curve used.

In addition, the plate distances must be converted to wave-lengths. This is done by using a portion of the neon spectrum and the results are shown in Fig. 3.

Once the plates have been calibrated, the remainder of the process lies in subjecting the phosphor to temperatures corresponding to those of liquid air, dry ice-acetone, room and boiling water while exposing the plate for the same lengths of time at constant slit widths. Figure 4 illustrates the emission spectra corresponding to the above temperatures with the intensity ordinate expressed in terms proportional to the number of photons per square centimeter per second per unit wave-length interval. Figure 5 is a similar set of curves but with the intensity ordinate expressed in terms of the number of photons per square centimeter per second per unit energy interval and the wave-length scale converted to energy units.

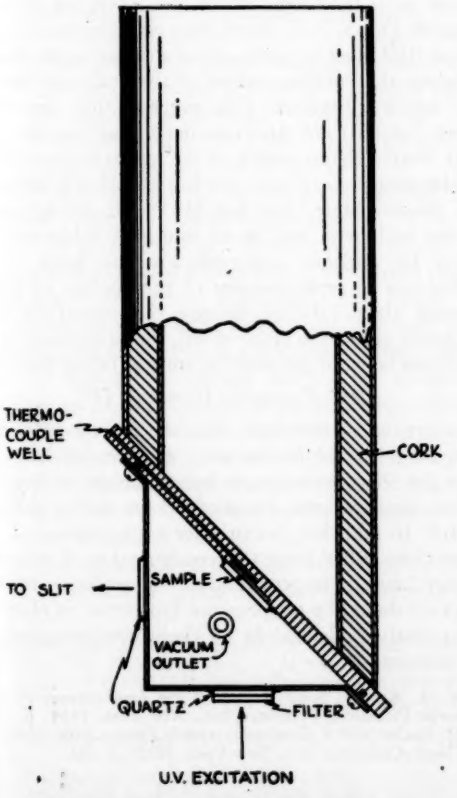

FIG. 1. The vacuum sample chamber.

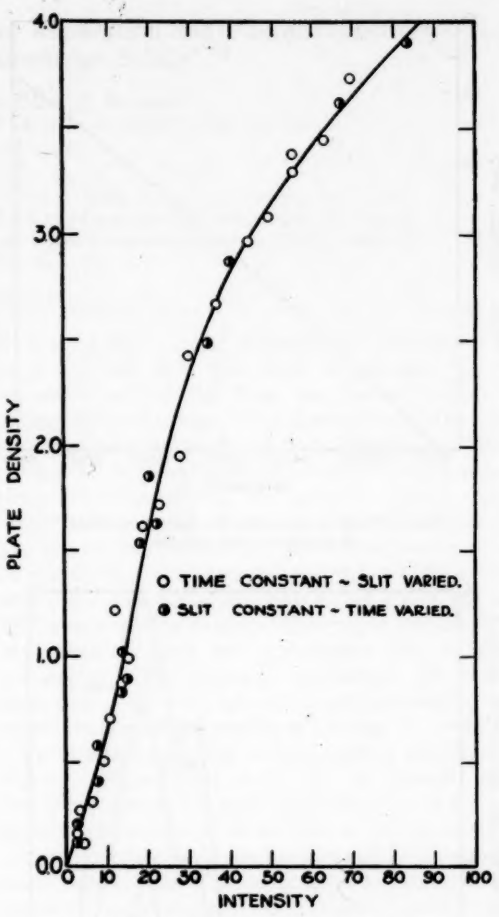

FIG. 2. Calibration curve relating plate densities to actual emission intensities.

RESULTS

The significant points to note in connection with the data are the following:

1. Five emission bands were clearly resolved between 6200A and 6800A.
2. The intensity of each band increases with temperature up to a critical temperature above which the luminescent efficiency of each band decreases rapidly.
3. The short wave-length peaks are relatively less intense at low temperatures.
4. The peaks of the individual bands shift slightly to shorter wave-lengths at the lower temperatures.
5. The half-widths of the individual bands increase with increasing temperature over the entire temperature range from −190°C to +90°C.

INTERPRETATIONS

The simple theory of broadening of emission lines by thermal vibrations indicates that above the Debye temperature and for strong coupling between the emit-

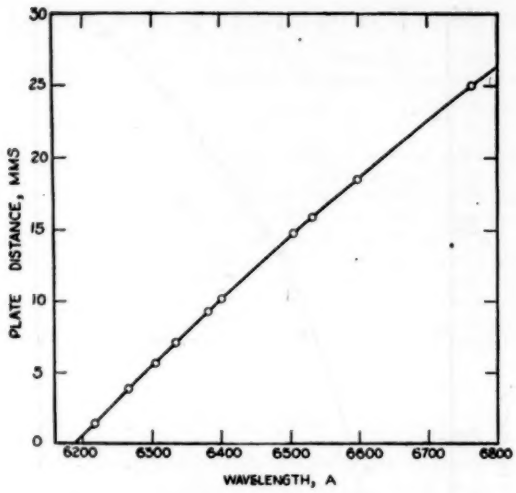

FIG. 3. Calibration curve for converting plate distances to wave-lengths.

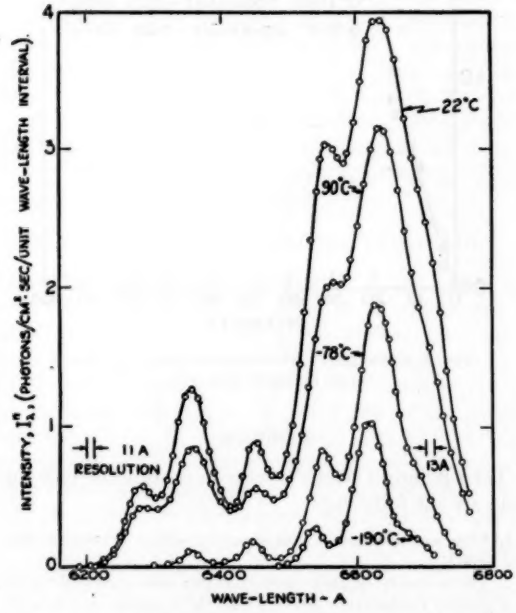

FIG. 4. The emission spectra of a manganese-activated magnesium germanate phosphor at various temperatures and with the intensity expressed as a function of wave-length.

ting state of the ion concerned and the lattice vibrations, the broadening is:[2]

$$\Delta\epsilon = (h\nu_0 \cdot kT)^{\frac{1}{2}}, \qquad (1)$$

[2] R. W. Gurney and N. F. Mott, Trans. Faraday Soc. 35, 72 (1939).

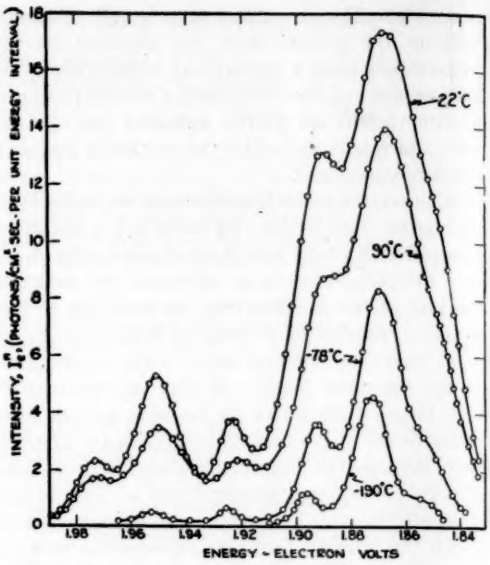

FIG. 5. The emission spectra of a manganese-activated magnesium germanate phosphor as a function of temperature and with the intensity expressed in terms of energy units.

where $h\nu_0$ is the energy of the line. Applying (1) to the data of Fig. 5, it is found that coupling constants of about 0.02 must be used, demonstrating weak coupling between the emitting states of the activator ion and the lattice vibrations. This suggests that the energy levels involved are relatively deep-lying and are probably largely characteristic of the free activator ion.

Manganese as an activator in phosphors is usually in the divalent state,[3] and free Mn^{++} has several excited states[4] each with five or six multiplet sublevels separated by energies approximately the same as the differences in peak energies of the spectra of Fig. 5, namely, about 0.025 ev. Because the separations of the sublevels are of the order of kT, the probability of the activator being in the emitting state J, rather than J_0 is:

$$P_J = P_{J_0} \exp[-(\epsilon_J - \epsilon_{J_0})/kT]. \qquad (2)$$

It is predicted, therefore, that the most intense emission band should be the long wave-length band and that the short wave-length bands should be negligible at low temperatures. These effects are shown in Figs. 4 and 5. In addition, because for each sublevel J configurations other than the configuration of minimum energy have finite probabilities, the emission for each sublevel should be temperature broadened as observed. Quantitative calculations on these interpretations are in progress.

[3] F. A. Kröger, *Some Aspects of the Luminescence of Solids* (Elsevier Publishing Company, Inc., New York, 1948), p. 58.

[4] R. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932), p. 283.

A Vacuum Ultraviolet Monochromator for Absorption and Photoconductivity Measurements on Luminescent Solids* **

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(Received April 28, 1949)

A vacuum ultraviolet monochromator for the region 1000A to 2000A is described in detail. The limited range makes rotation of the grating about a point and simplified construction feasible, since the loss of resolution at the extreme of wave-length is only 0.1 percent of the measured wave-length. The spectrum of the hydrogen source and a typical absorption curve are given.

INTRODUCTION

IN the study of the processes in luminescent materials the nature and the magnitude of the energy levels are of primary importance. To avoid experimental difficulties the luminescent material should use appreciable concentrations of the activator and should be susceptible to preparation in thin films. A simple ionic solid with these properties is manganese activated zinc fluoride, in which the energy levels can be determined by optical absorption, and the exciton and conduction states can be resolved by photoconductivity measurements. Hilsch and Pohl[1] and Schneider and O'Bryan[2] have shown that for the alkali halide semi-conductors and other simple halides, significant absorption bands lie in a restricted region between 1000A and 2000A. This limitation in range allows considerable simplification in the optical system and in the detecting equipment. This region also precludes the use of all materials except lithium fluoride in the optical path and makes a concave grating especially advantageous.

With a concave grating as dispersing medium conjugate foci lie on the Rowland circle through the central point of the grating surface. To maintain the source and detector slits of a monochromator at these focal points, if the source or detector is unwieldy and fragile, the grating itself must be moved along this Rowland circle. Baker[3] accomplished this in a grazing incidence instrument by moving the grating along a slot accurately machined to the Rowland circle. However, for a limited region the loss of resolution by defocusing is not too serious when the grating is simply rotated about a point on the Rowland circle. Powell[4] and Ferguson[5] employed this motion in normal incidence monochromators covering ranges of about 400A.

The resolution desired for possible fine structure[6] is 0.01 electron-volt or 1.5A which can be attained with a grating having a linear dispersion of 0.06 mm/A by using 0.05-mm slits. The losses of resolution by displacement of the slits from the Rowland circle at settings for the extremes of wave-length should be equal in energy units rather than in wave-length units. Then, the optical elements should be precisely on the Rowland circle at the setting for the midpoint of the energy range, 1200A, in the construction of this instrument. The loss of resolution at the short-wave extreme may be calculated roughly; at the setting for 900A, a point on the entrance slit is focused 0.8 mm behind the exit slit.[6] This results in an image of the point 0.04-mm wide at the exit slit for a loss in resolution of 0.7A, about 0.1 percent of the measured wave-length. The loss in resolution at the long-wave extreme is similar so that simple rotation of the grating is feasible.

Furthermore, this loss of resolution is produced by 0.01-inch displacement of the optical elements along the optical axis so the machining tolerances of the supporting structure may be as large as ± 0.003 inch. In addition, the adjusting mechanisms may be constructed more simply than the versatile and precise devices described by Sawyer[7] and Boyce,[8] and commonly found in the more elaborate instruments.

With these features simplifying construction, the monochromator has the optical elements, a grating and two slits, all mounted on plates closing the ends of the main supporting tube. For the source of radiation an end-on hydrogen glow discharge tube is used, and the detector is a 931-A or 1P21 photomultiplier tube. The detector is sensitized to ultraviolet by coating with a phosphorescent material.

DETAILS OF CONSTRUCTION

The body of the monochromator, shown in Fig. 1, is a brass tube having a wall-thickness of $\frac{1}{4}$ inch for rigidity, and having flanges hard-soldered around the ends. To these flanges are bolted the end-plates, which are machined parallel and serve as supports for the slits and grating. The vacuum seal between plate and flange is made by a flat gasket held in a groove in the flange to

* Presented at the Winter Meeting of the Optical Society of America in New York, New York, on March 10, 1949.
** Supported by the ONR through Contract N7onr-284, T.O. 1.
[1] R. W. Pohl, Proc. Phys. Soc. London 49, Extra Part 1, 3 (1937).
[2] E. G. Schneider and H. M. O'Bryan, Phys. Rev. 51, 293 (1937).
[3] R. F. Baker, J. Opt. Soc. Am. 28, 55 (1938).
[4] W. M. Powell, Jr., Phys. Rev. 45, 154 (1934).
[5] J. N. Ferguson, Jr., Phys. Rev. 66, 220 (1944).
[6] E. C. C. Baly, *Spectroscopy* (Longmans Green and Company, London, 1927), p. 161.
[7] R. A. Sawyer, J. Opt. Soc. Am. 15, 305 (1927).
[8] J. C. Boyce, Rev. Mod. Phys. 13, 1 (1941).

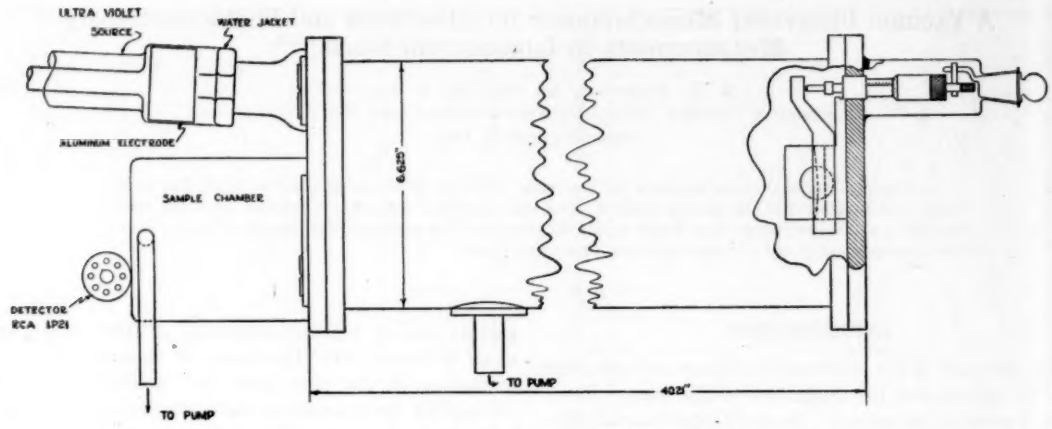

FIG. 1. The monochromator.

permit metal-to-metal contact, which, along with dowel pins, maintains the position of the end-plates and preserves the alignment of the optical elements. Silicone† rubber is used for the gasket material.

The grating, made at Johns Hopkins University, is glass with an aluminum reflecting surface[9] ruled lightly in a manner to give maximum intensity in the first order between 1000 and 2000A.[10] The 1.91-inch grating has a radius of curvature of one meter, and 15,000 lines per inch, for a linear dispersion of 0.06 mm/A.

The mounting for the grating, shown in Fig. 2, is essentially a holder pivoted to rotate about a vertical axis. The rotation is controlled by a standard micrometer head and a spring, parts 1 and 3 in Fig. 2. The wave-length of light at the exit slit is measured by calibration of the micrometer scale and the movement of the micrometer screw must be reproducible to 0.0001 inch for the desired accuracy in wave-length measurement. The micrometer head is held by an arm which is one piece with the bearing in which the grating holder rotates. The bearing, which is bolted to the inside of one of the end-plates, is large, sharply tapered and spring-loaded to eliminate play.

Motion of the grating about the horizontal axis is provided by set screws 8 and 9, holding the ring 6, in which the grating is clamped by a small threaded retaining ring, 7. Additionally, these set screws may be used for small focusing adjustments, moving the grating along the axis of the monochromator, although larger adjustments must be carried out with shims between the bearing piece 2, and the end-plate, to avoid moving the grating off the axis of the main bearing. To align the rulings of the grating with the axis of the main bearing, a vane from the holding ring 6, can be moved by set screws 10, rotating the grating about the axis of the monochromator.

The wide slitwidths permit very simple slits, shown with their mounting plates in Fig. 3 (a) and (b). The mounting plates 1 and 2, in Fig. 3, are machined to a thickness placing the slits on the Rowland circle at the setting for 1200A. The slit jaws are carried in ways cut in circular disks 3, which may be rotated by set screws 4, to align the slits with the rulings of the grating. The slit jaws are movable to permit the slitwidth to be set by feeler gauges. The mounting plate for the exit slit, Fig. 3(b), covers a slot 1.8 by 7.0 cm in the end-plate. The slot provides for replacing the slit with a film-holder, clamping the film on the Rowland circle to cover the region 950A to 2050A.

Scattered light in the monochromator is reduced by five baffles along the main tube and by painting baffles and the inside of the tube with carbon black in shellac. With an opening in the baffles large enough to illuminate the film slot, scattered light from the directly reflected image becomes troublesome at settings for 1400A and below. This difficulty is decreased by deposition of the sensitizing phosphor in front of the detector.

AUXILIARY EQUIPMENT

The sample chamber is a covered Pyrex glass cylinder having a depression in the back where light from the exit slit falls. Upon the bottom of this depression is deposited a layer of manganese activated willemite, about 0.004 gr/sq. cm. Immediately behind this depression a 931-A or 1P21 photomultiplier is clamped onto the sample chamber, and the layer of willemite enables this tube to respond to the far ultraviolet as in the scheme of Chevallier and Dubouloz[11] and Baker.[3] To measure photomultiplier current an RCA type WV-84A microammeter is used.

† Silastic No. 181 was generously supplied by the Dow-Corning Corporation, Midland, Michigan.

[9] G. B. Sabine, Phys. Rev. **55**, 1064 (1939).

[10] H. M. O'Bryan, Phys. Rev. **38**, 32 (1931).

[11] A. Chevallier and P. Dubouloz, Comptes Rendues **194**, 174 (1932).

The source of ultraviolet radiation is a hydrogen discharge tube adapted from Kistiakowsky's design.[12] It is of Pyrex and operates with 3- to 5-mm pressure of hydrogen at 0.7 to 1.2 amps. and 2200 volts from a reversed 5 kva commercial distribution transformer. The source is closed by a lithium fluoride window and sealed to the monochromator by a bell-shaped adapter and gasket. According to Schneider[13] lithium fluoride is suitably transparent to ultraviolet, although occasionally a layer of discolored material must be removed by polishing.

This window closing the source enables the pumping requirements to be handled by an oil-sealed rotary pump. According to Boyce[8] a pressure of 0.001 mm must be maintained and a Cenco Megavac with a speed of 0.5 liter per second at atmospheric pressure is adequate. An auxiliary pumping system is connected at the sample chamber.

Variations in the intensity of the source necessitate a means of interchanging a blank and the sample in the optical path quickly. Since the sample is deposited by evaporation as a thin film on a lithium fluoride plate, a blank is furnished by covering half the plate during deposition of the sample. By mounting the sample plate holder on a pivoted, counterbalanced arm, alternate switching of blank and sample into the optical path can be accomplished by properly located electromagnets. The magnets, outside the sample chamber, are energized

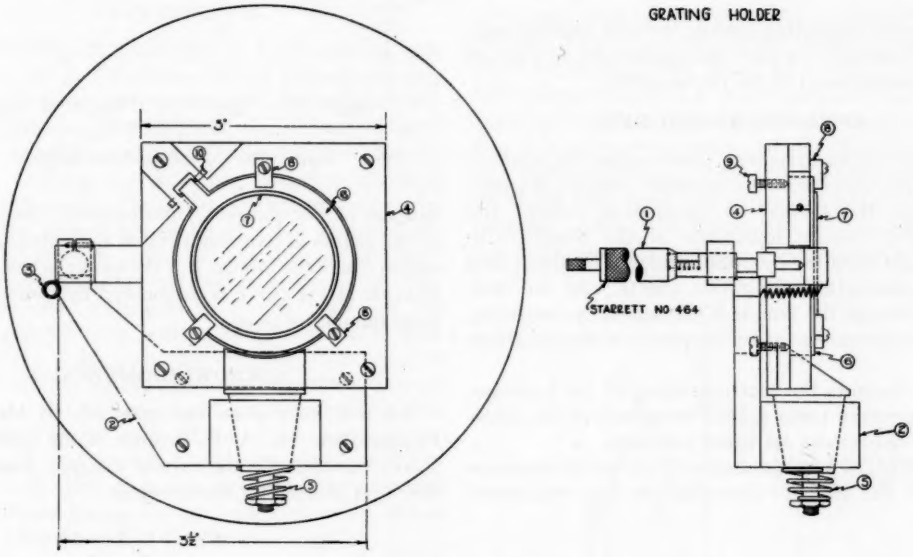

FIG. 2. The grating holder.

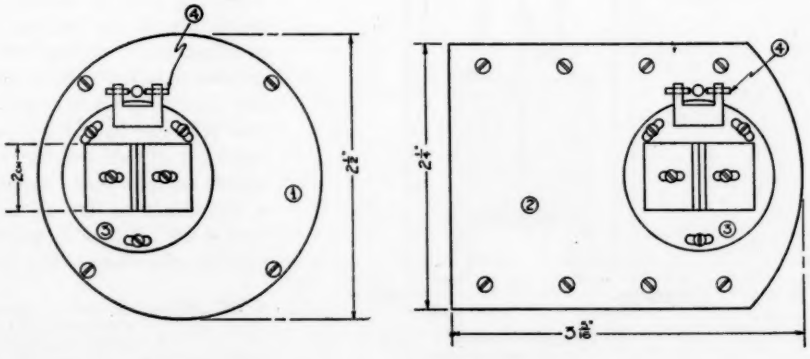

FIG. 3. The slit mechanism.

FIG. 3a FIG. 3b

[12] G. B. Kistiakowsky, Rev. Sci. Inst. **2**, 549 (1931).
[13] E. G. Schneider, Phys. Rev. **49**, 341 (1936) and J. Opt. Soc. Am. **27**, 72 (1937).

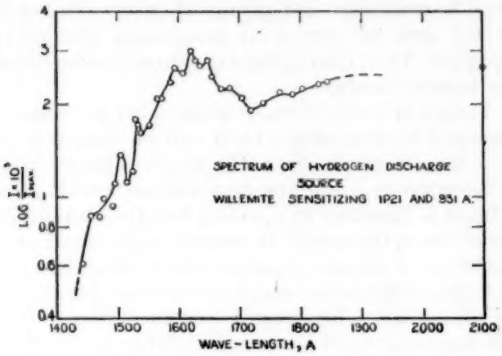

FIG. 4. The spectrum of the hydrogen discharge source.

by 110 volts alternating current to avoid residual magnetic fields around the photomultiplier tube, and are off during measurement of the photocurrent.

APPLICATIONS AND DATA

The scheme for measuring photoconducting states in conjunction with the monochromator, consists of applying across the sample an alternating voltage and modulating this by irradiation of the sample with pulsed light from the hydrogen source. The alternating voltage eliminates polarization effects, and the dark current through the sample is eliminated by measuring only the photocurrent at the frequency of the pulsations of light.

Figure 4 shows the spectral output of the hydrogen discharge source using a 1P21 sensitized to the ultraviolet by manganese activated willemite.

Typical of the data obtained with the monochromator is Fig. 5, the absolute absorption of two evaporated

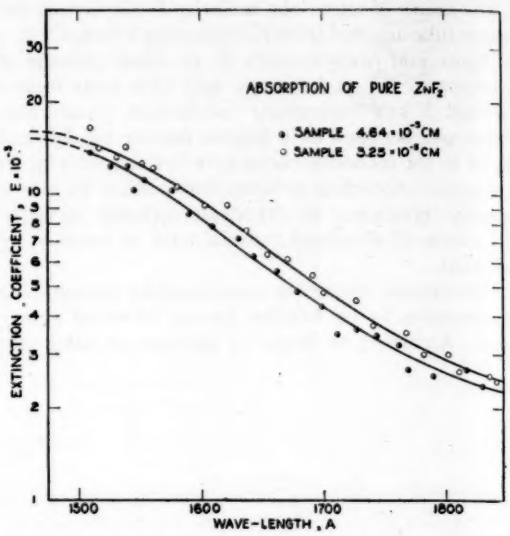

FIG. 5. The absorption of zinc fluoride.

samples of zinc fluoride. Unfortunately, the scattering of the points is representative of data obtained in the region where the intensity of the source is low. The best location of the curve is established by measuring at a large number of points.

ACKNOWLEDGMENTS

We wish to express our gratitude to Mr. N. DiCostanzo and Mr. A. R. Bennett of the University of North Carolina for the careful machine work and to Mr. S. H. Patten for the drawings.

Thermoluminescence of Manganese-Activated Zinc Fluoride Phosphors*

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(Received April 28, 1949)

Thermoluminescence measurements at linear heating rates of 0.025 and 0.100 K°/sec. on the ZnF_2:Mn phosphor with electron and ultraviolet excitation have been made as a function of activator concentration and crystallization temperature. Five individual glow peaks between 100°K and 700°K have been clearly resolved. The relative intensities and widths of the peaks are independent of the type of excitation and activator concentration but are strongly dependent on crystallization temperature and subsequent annealing. A detailed theoretical analysis of the glow peak at 350°K with the 0.025 K°/sec. heating rate indicates that the most probable mechanism of the kinetics is basically first order with a strong probability of retrapping. The depths of the electron traps responsible for the complete thermoluminescence are estimated, and the possibilities of the precise physical nature of individual electron traps in ZnF_2:Mn are discussed in the light of the glow data.

INTRODUCTION

THERMOLUMINESCENCE measurements, first reported by Urbach[1] and Wick[2] and subsequently refined and theoretically analyzed by Randall and Wilkins,[3] Williams and Eyring,[4] and Garlick and Gibson,[5] are well established as a useful method of investigating the long, temperature dependent phosphorescence of luminescent solids. The glow experiment consists of exciting the phosphor, usually at a low temperature; allowing the emission to phosphoresce to a low intensity; and then measuring the emission intensity as the phosphor is heated, preferably at a linear rate. In this project, because slow heating rates produce thermoluminescence data with the emission from electron traps of different depths more clearly resolved, rates of 0.025 and 0.100 K°/sec. were used. Because ZnF_2:Mn consists of a simple ionic lattice with a substitutional activator, it was expected that the consequent simplicity of the thermoluminescence would be amenable to quantitative theoretical analysis, even to the precise physical identification of the electron traps.

APPARATUS

The apparatus is shown in Fig. 1. The powdered ZnF_2:Mn is deposited by settling on an aluminum plate which is attached to the bottom of the cavity in the copper block. The block is inverted and lowered into the glass Dewar apparatus making a vacuum seal at the outer edge of the cavity. The phosphor is now situated so that, when liquid air is added to the inner chamber surrounding the copper block and the double jacket is evacuated, radiation as well as conduction is primarily from the copper block. The ZnF_2:Mn is then excited either by 2537A and 1849A radiation through the quartz plate at the bottom of the apparatus from a 500-watt mercury discharge lamp or from a high voltage electron discharge from one of the leads at the bottom. After phosphorescence to a low emission intensity, the linear heating rate is accomplished by scheduled regulation of the current through the coil around the block. The emission intensity is measured by the 1P21 photomultiplier tube under the quartz window, and the temperature is determined from the thermocouple inside the block near the sample. This apparatus was used

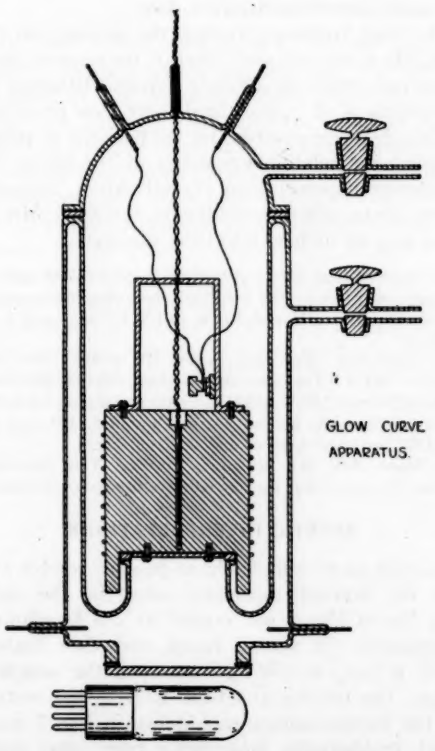

FIG. 1.

* Supported by the ONR through Contract N7onr-284, T.O. 1.
[1] F. Urbach, Wien. Ber. (IIA) **139**, 363 (1930).
[2] F. G. Wick, Wien. Ber. (IIA) **139**, 497 (1930).
[3] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. **A184**, 366 (1945).
[4] F. E. Williams and H. Eyring, J. Chem. Phys. **15**, 289 (1947).
[5] G. F. J. Garlick and A. F. Gibson, Proc. Phys. Soc. London **60**, 575 (1948).

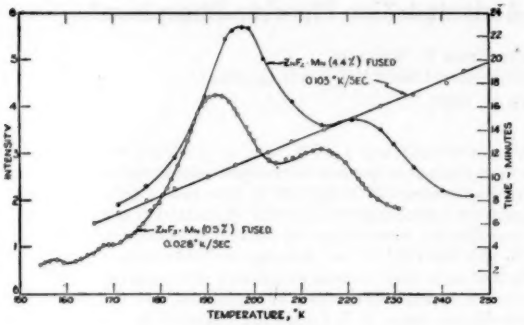

FIG. 2.

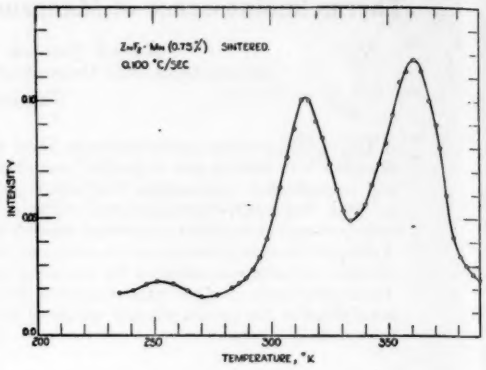

FIG. 3.

from 100°K to 400°K; a slightly modified apparatus was used from 300°K to 700°K.

EXPERIMENTAL RESULTS

Variation of activator concentrations between 0.5 and 5 mole percent Mn has negligible effect on the relative numbers of electron traps of different depths if the crystallization temperatures are the same. Incidentally, the difference in peak positions in Fig. 2 results from the different heating rates. A typical heating curve is also shown to demonstrate the linearity.

Ultraviolet and electron excitation yield essentially the same thermoluminescence data.

The heat treatment during the preparation of the ZnF_2:Mn has a profound effect on the relative numbers of electron traps of different depths. Although slight indications of all five of the definite glow peaks shown in Figs. 2–4 were observed for the majority of phosphor samples, the relative intensities of the peaks varied immensely depending on crystallization temperature during preparation. Accordingly, the ZnF_2:Mn phosphors may be divided into three classes:

(1) Sintered ZnF_2:Mn crystallized between 700 and 850°C (the m.p. is 870°C). The principal thermoluminescence of the phosphor peaks at 315 and 360°K (0.100 K°/sec.) and is shown in Fig. 3.

(2) Fused ZnF_2:Mn crystallized at 870 to 900°C but not subjected to 1000°C. The most intense glow peaks of this phosphor occur at 198 and 221°K (0.103 K°/sec.) and are shown in Fig. 2, but in addition, the less intense peaks at 315, 360, and 610°K (0.093 K°/sec.) are observed and shown in Fig. 4.

(3) Fused ZnF_2:Mn heated at 1000°K. This phosphor resembles (2) except that the low temperature peaks are absent.

KINETIC INTERPRETATIONS

In order to as completely as possible resolve a glow peak for detailed theoretical analysis, the sintered ZnF_2:Mn of Fig. 3 was excited at 298°K, allowed to phosphoresce for several hours, and then heated at 0.0255 K°/sec. to 350°K, whereupon the sample was chilled. The heating at 0.0255 K°/sec. was restarted, and the thermoluminescence shown in Fig. 5 was obtained. Incidentally, interference from other traps is not completely eliminated on the high temperature side where a small glow peak is known to exist from other measurements. However, deductions on the kinetics can be made.

The peak position of the glow curve for the partially exhausted electron trap is 4 K° higher than the original peak. This could be interpreted as evidence for a slight distribution of trap depths, but a shift of 4 K° should be accompanied by a detectable decrease in half-width. Since the decrease was not observed, it is concluded that a single trap depth or a very narrow distribution of trap depths is responsible for the glow peak of Fig. 5.

As shown in Fig. 5, the simple first order theoretical glow curve obtained using the electron trap depth and the frequency factor yielding the correct half-width and peak position fails to fit the initial part of the experimental curve. Also, the shift in peak positions for the two rates of heating is predicted by the first order mechanism to be 16 K°, whereas 13 K° is observed. Clearly, the simple first-order mechanism is not completely applicable.

A simple second-order mechanism also does not seem applicable. Again the theoretical shape and dependence of peak position on rate of heating is not in agreement with experiment. Also, a second-order theory would

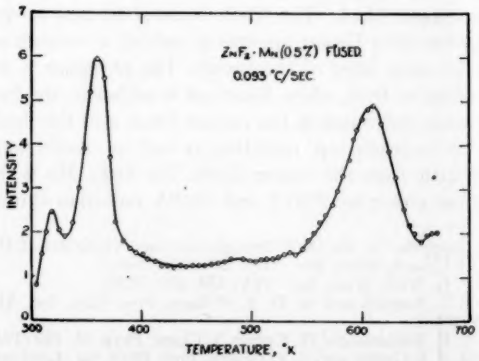

FIG. 4.

require a recombination of conduction electrons and centers slow enough to maintain an equilibrium of electrons between the traps and the conduction band. The experimental intensity of emission is too great for such an equilibrium to be maintained with the theoretical trap depth required to approximately fit the glow data.

The possibility of retrapping must, therefore, be invoked. The curve calculated for equal probability of emission and retrapping and shown on Fig. 5 provides a good fit. Incidentally, the accompanying equation on Fig. 5 is strictly correct only if there are no important deeper traps in this phosphor. The objections to this mechanism are that again the dependence of peak position on heating rate is not accurately predicted and the frequency factor required is $5\times10^{12}T$, which suggests an unlikely chain mechanism.

The most likely mechanism seems to be that emission is more probable than retrapping, about 1.5 times as probable. This leads to a trap depth of 24 K'cal.; a frequency factor of $10^{10}T$, or about kT/h, which is quite reasonable; and predicts the proper shift of peak position with partial exhaustion and the correct dependence of peak position on rate of heating. Although there is no assurance that the mechanisms for the other four electron traps are the same, the approximate depths are presented in Table I according to this interpretation.

THE NATURE OF ELECTRON TRAPS

Some possibilities of the physical nature of the electron traps responsible for the thermoluminescence of ZnF_2:Mn may be mentioned. The reducing action of the phosphor on acid permanganate or chlorine water indicates an excess of zinc and suggests the presence of halide vacancies. A relatively large concentration of both in the fused phosphors could account for the low and high temperature glow peaks not found in samples crystallized at lower temperatures. The vacancies are probably the deep traps; and self-trapping in the neighborhood of zinc atoms may account for the shallow traps. Consistent with the latter interpretation is the observation that the sample fired at 1000°C, at which temperature zinc atoms would be expelled, did not exhibit the low temperature traps. The electron traps responsible for the thermoluminescence just above room temperature could result from surface states, which sintering might be expected to enhance.

TABLE I.

Temp. peak emission (K°) with 0.1 K°/sec.	198	221	315	360	610
Estimated trap depth (K'cal.)	12.9	14.4	21	24	42

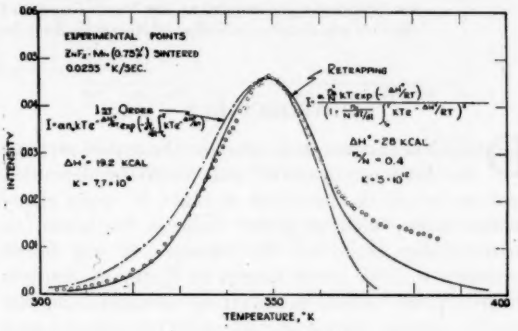

FIG. 5.

CONCLUSIONS

Data from thermoluminescence measurements on samples of manganese activated zinc fluoride of various concentrations and heat treatments are presented. Several electron traps exist, and the principal factor determining the glow curve of a sample is its heat treatment during preparation. Analysis of experimental results indicates a first-order process modified by a strong probability of retrapping as the most likely mechanism. Estimates of the various trap depths are given, and speculation as to their physical nature is presented.

Acknowledgment is made to Stanley H. Patten for the preparation of the figures, to Peter D. Johnson for chemical analysis of many of the samples, and to both of these and to other members of the project for cheerful assistance in the performance of some of these experiments.

Photometric Evaluation of Luminous Materials for Naval Uses

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(Received April 22, 1949)

Types of luminous materials being used by the Navy are given in brief outline with some mention of particular application to problems arising under dark or near-dark conditions. The program for improving low brightness photometry at the Naval Research Laboratory is explained with special attention given to physical photometry, utilizing photo-multiplier tubes.

INTRODUCTION

DURING the war need arose in the armed services for luminous material that could be depended upon as an aid in operations at night or, when emergencies arose, such as power failures, blackouts, or abandon ship activities. For example, it was found necessary to have some system of luminous markers aboard Naval vessels to facilitate operations on the weather deck at night or to aid landing operations under cover of darkness. Such markers not only acted as safety aids but permitted operation of vessels under very difficult circumstances. Luminous markers, instrument parts, dials and instrument panels were used successfully.

Figure 1 gives an outline of the types of materials and the more important uses in Naval service. The phosphors used in these materials are the sulfides of calcium, strontium, and zinc with various activators to give good brightness, color and decay characteristics with durability sufficient for use under sea conditions. Organic luminous materials are used where high brightness is desirable and durability not so important.

PHOTOMETRY AT LOW BRIGHTNESS

The brightness of the materials as outlined in Fig. 1 is ordinarily low; due first to the nature of the material, second to the desire to escape enemy observation, and third to preserve the dark adaptation of the eyes of the personnel working within visual range of a marker.

Practically all photometric measurements for the evaluation and purchase of large quantities of such materials by the Navy during the war were made visually. Either some commercially available photometer such as the Macbeth illuminometer was modified to fit the type of measurement or especially designed photometers with visual angles up to 10 degrees were used. These were fitted with color matching optical filters in order to avoid the difficulties of heterochromatic photometry. The largest portion of the materials purchased by the Navy contained a zinc sulfide phosphor having a "radioactive green" color and a filter combination was used in the photometer to give a color match. A Jena GG11 (2 mm) and BG12 (1 mm) filter was found satisfactory for such color matching. The photometers were either calibrated by the National Bureau of Standards or by laboratory personnel using a set of standard lamps calibrated at the Bureau.

By modifying the available photometers and introducing a single filter which matched certain colors reasonably well, it was possible to use fairly simple photometric equipment and methods. This equipment enabled the manufacturers to make at least a preliminary evaluation of their material and to assist in the control of phosphor production.

It was possible to get fair agreement between the various laboratories but no definite visual photometric apparatus or method was developed to enable the average laboratory technician not trained in low intensity photometry to get accurate results. Development of phosphors of varying colors added to this difficulty. Furthermore, since much of the luminous material used by the Navy has a brightness range where the Purkinje effect is most pronounced, it is quite difficult for even the experienced photometrist to get consistent results especially with phosphors of different colors.

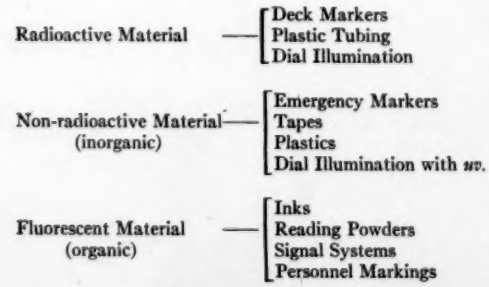

FIG. 1. Brief outline of luminescent materials and their uses.

DEVELOPMENT OF PHYSICAL PHOTOMETRY

In all photometric work the calibration of a photometer must eventually refer back to visual comparison with an accepted standard. The methods of physical photometry, however, offer possibilities of avoiding many of the difficulties of visual photometry and at the Naval Research Laboratory such photometers utilizing the 1P21 and 1P22 photo-multiplier tubes are being developed.

Filters to give the multiplier tubes a sensitivity curve closely approximating that of the human eye over several points in the Purkinje region have been de-

veloped[1] and within certain limits it is possible to get reasonably accurate and reproducible results at low brightness values with phosphors varying in spectral characteristics. The inconvenience of inserting different filters at different brightness levels is a practical difficulty which can possibly be reduced by further consideration of color variations.

In order to provide standards of brightness with which to calibrate the photoelectric photometer it was necessary to find a combination of a tungsten lamp and optical filter which gave a color approximating that of the phosphor to be studied.

In Fig. 2 is shown a set of filters which arbitrarily divide the visible portion of the spectrum into four color groups. In each case the temperature of the tungsten can be varied, but ordinarily a color temperature of approximately 2600°K is used. From this set an approximate color match with most of the ordinary phosphors can be obtained and with phosphors of relatively high excitation purity, only four calibrations of the photometer are made necessary with a given correction filter. This additional filter is chosen to give a spectral correction at a point between scotopic and photopic levels and is used to reduce the error in calibration due to slight differences in color between the phosphor and the filter-tungsten source giving the best match.

When phosphors are mixed to give more complex spectral distributions, separate calibration curves, of course, are necessary for best accuracy but since any calibration is made in terms of effective microlamberts (2360°K source), every additional calibration is quite tedious and can only be effected each time by using many observers and statistical methods. For mixtures that give "white" screens, etc., a fifth filter of Corning Daylite No. 5900 is used with a tungsten lamp to give an approximate color temperature of 6000°K.

[1] W. S. Plymale, Jr., "Filters for spectral corrections of multiplier photo-tubes used from scotopic to photopic brightness levels," Rev. Sci. Inst. 18, 8 (1947).

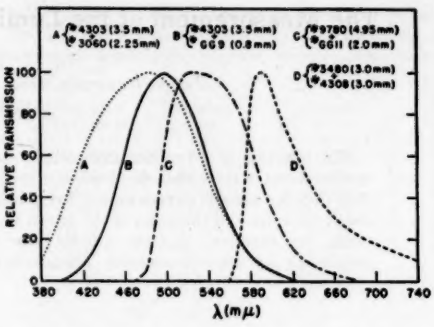

FIG. 2. Photometric matching filters for phosphors most commonly used in luminous markers and other materials.

When the control of the manufacture of the phosphorescent material permits reproducible colors a separate calibration for each phosphor type is possible.[2] Once the photoelectric photometer calibration is made, a slight adjustment of the multiplier dynode voltage will maintain this calibration. Results are at least reproducible which is not always the case in visual photometry.

SUMMATION

Briefly, it may be stated that physical photometry will prove more satisfactory than visual photometry for evaluation of luminous materials where repeated brightness, color and decay measurements are to be made. As yet, the accuracy of a photometer based on the method described above has not been fully determined and the filters, including the choice of a correction filter for the tube itself, are tentatively chosen. It is hoped that complete data and a full photometric discussion of such a photometer can be given soon in a separate paper.

[2] J. R. DeVore, "Calibration of a photo-multiplier photometer," J. Opt. Soc. Am. 38, No. 8 (1948).

The Measurement of the Luminescence of Fluoroscopic X-Ray Screens*

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(Received April 13, 1949)

The selection of a superior fluoroscopic screen for direct x-ray observation and diagnosis requires the measurement of the visual effectiveness of the shadows of objects on the screen. At clinical levels of excitation ZnS-CdS fluoroscopic screens are excited to brightnesses near the condition of cone to rod transition. At these levels the color and thickness of the screen becomes critical. A series of screens of various colors and thicknesses was examined, and the optimal color and thickness was determined with the aid of an apparatus permitting psychometric technics. The selected screen provides cone stimulus in nearly all clinical situations.

I. INTRODUCTION

FLUOROSCOPIC x-ray screens are used in medical diagnosis. Because the x-rays can be harmful, these screens are activated to only a very low brightness level. The activating energy at the screen varies from several roentgens per minute in studying the hands, feet, or neck, down to as little as 10 milliroentgens per minute through the abdomen of a very heavy patient. The usual clinical intensity at the screen is about 300 to 30 milliroentgens, and these intensities result in screen brightnesses from 4.0 to 0.4 microlamberts as reported by W. E. Chamberlain in 1942.[1] Such brightnesses are close to, or below, the rod-cone transition point, which is variable, depending upon the color and shape of the object, but which was reported in 1939 by Hecht as about two and one-half microlamberts in the perception of extended fine lines.[2] A great deal of improvement in fluoroscopic perception might be anticipated if the brightness of the screens, in clinical use, could be raised to a level slightly above the rod-cone transition. Coltman has described an electronic brightness amplifier which would do much more than this,[3] but until it is completed and marketed, even a small improvement in fluoroscopic screens for direct observation would be very useful.

Fluoroscopic screens usually consist of zinc and cadmium sulfides, activated by a heavy metal, such as silver. An improvement of these screens might be expected by changing the proportions of the cadmium and zinc, or changing the thickness. Increasing the cadmium turns the emission of the phosphor more yellow, eventually making it too yellow to be useful at low brightnesses near the rod-cone threshold, because of the Purkinje phenomenon. Increasing the thickness makes the screen brighter, but would result eventually in blurring and loss of resolving power. The selection of the best screen, therefore, becomes a problem of measuring the actual visual performance, rather than only apparent brightness, in an excitation range comparable to the clinical applications of the screen.

II. EXPERIMENTAL RESULTS

An apparatus has been constructed which permits psychometric methods of measurement of resolving power of the screens at various contrasts and brightnesses. This apparatus is shown in Fig. 1. It consists of a lead plate pierced with 16 round one-inch holes. Over each hole is placed an aluminum block, containing a pattern of three very small holes, arranged in a row, whose orientation is set in a random sequence. For each set of 16 blocks, all of the same thickness, the three holes per block are varied logarithmically in diameter from block to block. This provides the necessary logarithmic variation of stimulus required for this psychometric method. The assembly of blocks and lead plate is curved to the surface of a sphere whose center is at the x-ray tube, so that the x-rays are nearly parallel to the axes of the small holes. An additional layer of aluminum serves to control the final brightness and contrast at which the shadows of the small holes will appear on the screen as brighter spots. The observer is required to record his perception of the orientation of the small patterns of spots on a recording tablet provided with guides to permit him to work in the darkness. He makes this record under the conditions for forced guessing, in which he must make some answer for each of the illuminated areas on the screen. Each of the screens studied is presented with the same combinations of thicknesses of aluminum, intensities of x-ray, and number of presentations. In all cases, the observer is dark-adapted before making measurements for at least 15 minutes, which is adequate for the brightnesses involved.

Several combinations of contrast, hole size, and x-ray intensities were used, varying from about six roentgens per minute, which is above normal clinical levels, to one-half milliroentgen, which is below the clinical levels of excitation. The brightness of the screen for this variation is from about 480 to about two hundredths

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** This research was partially financed by a Grant-in-Aid of Research to the Temple University Hospital from the United States Radium Corporation. The experimental screens were prepared by this corporation.

[1] W. E. Chamberlain, "Fluoroscopes and fluoroscopy," Radiology 38, 383 (1942).

[2] S. Hecht and E. U. Mintz, "The visibility of single lines at various illuminations and the retinal basis of visual resolution," J. Gen. Physiol. 22, 593 (1939).

[3] J. W. Coltman "Fluoroscopic image brightening by electronic means," Radiology 51, 359 (1948).

microlamberts. Within this range there were several values. It is not essential to measure exactly either the x-ray intensity, apparent visual brightness, or visual contrast, on the various fluoroscopic screens by this method, since all screens will be compared under the same series of excitation conditions. Our purpose is to select the best screen in terms of statistically established visual performance.[4]

Screens of seven ZnS to CdS ratios were examined. Figure 2 shows the computed colorimetric specifications plotted on the ICI color mixture diagram.[5] Computations from the spectral traces of the activated screens were made with respect to "Equal Energy," since the screens act as sources of light. It can be seen that a smooth curve can be drawn through the colorimetric coordinates of screens at various ZnS to CdS ratios.

The curve shows the increase of yellowness in the emission of the screen, as the cadmium content is increased. The screen numbered one has the most zinc, that numbered seven has the most cadmium. Screen number eight is a commercial fluoroscopic screen, comparable to the screens studied by Chamberlain in 1942.

A preliminary examination by the method of paired comparison showed that one of these seven ratios seemed the most useful. The screens were placed side by side, in pairs in a regular clinical x-ray fluoroscope, over a 4×5-inch plastic placque containing a series of copper wires imbedded in paraffin. The diameters of these wires were 0.8, 0.5, 0.36, 0.2, 0.13, 0.10, 0.08, and 0.06 millimeters. A large piece of lead glass was placed over the assembly to protect the observer. That screen, of each pair, by means of which the wires could be best visualized, was rated as better. From the completed comparison in pairs, screen number five was selected.

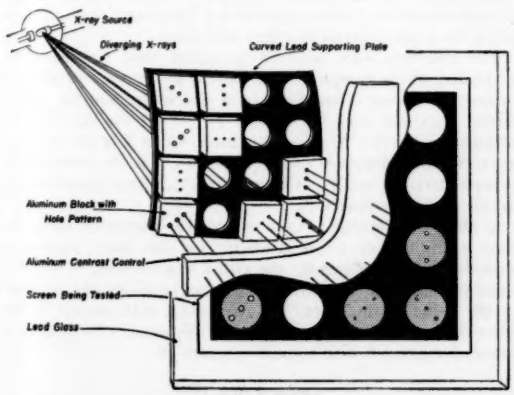

FIG. 1. Contrast-Acuity apparatus used in studying the visual effectiveness of fluoroscopic screens.

[4] See Appendix I for further description of the contrast acuity apparatus.

[5] W. H. Byler and C. C. Carroll, "A method of determining the chromaticity of fluoroscopic material," J. Opt. Soc. Am. 35, 258 (1945).

TABLE I. Visual effectiveness relative to screen 16. Computed from frequency of seeing, corrected for chance guessing.

Screen	Relative effectiveness	ZnS-CdS ratio	Thickness inches	Dominant wavelength
8	0.83	*B*-1	0.0095	553
10	0.86	59/41	0.0095	560
11	0.96	55/45	0.0095	566
16	1.00	55/45	0.0125	566
17	0.92	52/48	0.0125	574
19	1.00	55/45	0.0095	566
20	1.20	55/45	0.0125	566
21	1.12	55/45	0.0160	566

The phosphor of this screen had the ratio of 55 parts of zinc sulfide to 45 parts of cadmium sulfide.

Additional screens were then prepared using this ratio and the ratios on each side of this. The screens were coated at two thicknesses, 0.0095" and 0.0125".

These screens were examined with the psychometric device shown in Fig. 1, with the results shown in Table I. Since the method allows the measurement of the visual acuity, in a sense, that the screen provides, the performance of the screens has been rated in terms of visual resolving power relative to screen 16. The comparison of these scores for screens numbered 10 and 11, and 16 and 17, shows that the ratio 55/45 results in the best visual performance. The comparison of screens 11 and 16 shows that the thickness of screen 16 is better. The color of the phosphor thus found to be most visually efficient is quite different from that of the presently available fluoroscopic screens such as screen number 8. The dominant wave-length is 566 millimicrons instead of 553 millimicrons. This color is quite yellow, as compared to screen number 8, being best represented by the Munsell designation 4 GY, as compared to 8.5 GY.

Three new screens were then prepared, using the ZnS to CdS ratio of 55/45. The phosphor was prepared with some chemical and mechanical improvement over the previous mixture, and coated at three thicknesses. These screens, numbered 19, 20, and 21, were compared with screen 16 in a shorter series, with the results shown in Table I. The phosphor ratio 55/45, at the thickness of 0.0125 inch, is found to produce the best screen in the series here reported. The clinical brightness range of this last screen, as estimated from illuminometer measurements, would be from about 21 to about 2.0 microlamberts, as compared to the 4.0 to 0.4 previously reported. In only extreme cases of clinical fluoroscopy, will it be necessary to work below the rod-cone transition brightness, and in these cases the fluoroscopist can expect to maintain the cone level, by only a very moderate increase in x-ray excitation intensity.[6]

III. STATISTICAL ANALYSIS

The purpose of the statistical analysis by means of the chi-square technique, is to determine if enough meas-

[6] See Appendix II for the measurement of certain other screens.

TABLE II. Chi-squared test for statistical significance of differences.

Comparison	Visual performance	Number of measurements	Probability value	Interpretation
16 vs. 8	1.00 to 0.83	336	0.0016	different
16 vs. 17	1.00 to 0.92	336	0.089	not established
16 vs. 20	1.00 to 1.20	48	0.032	different

urements have been made to establish the differences found as not dependent upon chance.[7] When the differences are large, only a few measurements need to be made, but when the differences are small, a great many measurements may be statistically demanded.

From Table II, we see that the number of measurements, 336, for each screen, suffice to show that screen number 16 is significantly different from screen number 8. This is evidenced by the value of the probability of divergence from association, which is less than the critical value of 5 percent. The difference between screens 16 and 17 is much less, and if a critical decision were required for choice between the screens, more measurements would have to be made. Another way to interpret the difference between 16 and 17 would be to say it is too small to be significant. The comparison between 16 and 20 shows screen 20 to be such an improvement over screen 16 that the difference found is established by only 48 measurements.

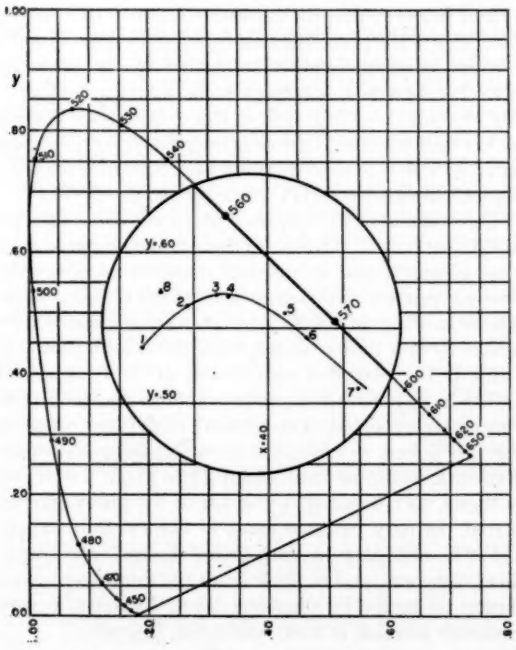

FIG. 2. I.C.I. Chromaticity diagram showing the locus of various ZnS-CdS ratios in fluoroscopic screens. The relevant portion of the diagram has been enlarged 2½ times.

[7] G. U. Yule, *An Introduction to the Theory of Statistics*, (C. Griffin & Co., London, 1936), pp. 380 and 388.

TABLE III. Physical values of the contrast-acuity apparatus.

X-ray tube values KVP	ma	X-ray at screen mr/min.	X-ray contrast	Hole plate mm Al	Contrast plate mm Al	Drill sizes of holes B & S gauge
92	3.5	6270	0.257	0.51	0.43	56 65 72 77
85	1.0	1350	0.156	0.51	3.18	56 65 72 77
90	3.0	456	0.226	3.18	15.88	42 51 56 65
90	1.5	194.5	0.255	3.18	15.88	42 51 56 65
46	2.0	3.0	0.820	12.70	25.40	30 42 51 56
40	1.5	0.55	0.855	12.70	25.40	30 42 51 56

IV. SUMMARY

We have found that the selection of the best fluoroscopic screen can be based upon the measurement of visual performance directly, instead of by inference from the screen brightness. The visual performance can be made by a psychometric technique, to which statistical analysis for significance of differences is readily computed. The screen so selected has a ZnS to CdS ratio 55/45, which produces a color somewhat yellower than previous fluoroscopic screens. This phosphor must be used at an optimal thickness, since too thin a screen shows poorer performance due to lack of brightness, and too thick a screen shows poorer performance due to lack of resolving power.

APPENDIX I

Details of Visual Resolution Apparatus

The apparatus shown in Fig. 1 of the text was developed from that of Rose.[8] It consisted of four combinations of aluminum thicknesses. These combinations are indicated in Table III, which also shows the drill sizes used in making the sets of holes in the "hole plates." In use, the x-ray intensity was determined directly for each condition of observation with a Victoreen "*r*-meter," from which the x-ray contrast has been computed.

The observers were required to record their guesses of the orientation of the groups of three holes. This record was corrected against the actual orientation, from which the number "*R*" of correct responses was determined. To correct for guessing, the formula $S=R-(T-R)/(N-1)$ is used, where S is the corrected score, R is the number of correct responses, T is the total number of presentations, and N is the number of identical presentations. In this study N equals four.

In these measurements each screen was compared under the same conditions of x-ray intensity, for the same number of presentations. Consequently the visual effectiveness, in terms of visual resolution at the contrasts used, can be effectively expressed by the value of the score "*S*," as a ratio with respect to any selected screen. In the present paper, this visual effectiveness of screens is expressed with respect to screen 16.

APPENDIX II

Summary of All Screen Measurements

Series One.—This series consisted of seven screens, varying in ZnS-CdS ratio, coated on hard paper stock at the thickness of

[8] A. Rose, "Sensitivity performance of the human eye on an absolute scale," J. Opt. Soc. Am. 38, 196 (1948).

TABLE IV. Paired comparison of ZnS-CdS ratios.

Screen	ZnS-CdS ratio	Rank order for wire object	Brightness μL at 200 mr/min.
1	64/36	seventh	61
2	61/39	fifth	72
3	59/41	fourth	74
4	57/43	sixth	82
5	55/45	second	83
6	535/465	first	78
7	52/48	third	80

0.0140 inch. These screens were examined only by paired comparison with the results shown in Table IV.

Screen No. 6 showed the best visualization of a series of wires in a plastic plaque (see text), but the difference between the effectiveness of No. 6 and No. 5 was very small. Screen No. 5 showed somewhat greater apparent brightness when measured with a MacBeth Illuminometer provided with a matching greenish Wratten Filter.

Series Two.—This series consisted of two thicknesses (0.0095-inch and 0.0125-inch) and four ZnS-CdS ratios (64/36; 59/41; 55/45; and 52/48). These screens were numbered 9 to 12 for the thinner series and 14 to 17 for the thicker series. From the paired comparison method it was easy to determine that screens 9, 12, 14, and 15 were less satisfactory. Consequently absolute measurements were made only with screens 10, 11, 16 and 17, with the results shown in the text as relative visual effectiveness with respect to screen 16.

Series Three.—This series consisted of three thicknesses of the 55/45 ratio, numbers 19, 20, and 21, whose performance is discussed in the text. Screen No. 20 was found to be the best screen.

Series Four.—Coincident with the preparation of the experimental screens, a series of screens were obtained from commercial sources, made by the Patterson Screen Division of the E. I. du Pont de Nemours and Company. These screens were numbered consecutively to their date of purchase, over a period of two years. Screen numbers 8 and 13 were labeled "B-1" by the manufacturer, and can be considered comparable to those described by Chamberlain in 1942. The other screens were labeled "B-2," and are numbered 18, and 23 in the tables below. The color of all of these screens is apparently the same as number 8, as indicated in Fig. 2. In addition a new greenish screen of similar color and thickness was prepared, and numbered 22. The performance of this fourth series is shown below in Table V, with a general summary of the performance of all the screens. The green screen No. 22 is not significantly different from number 16 nor from the most recently purchased screen No. 23. The independent improvement of the Patterson screens during the course of these investigations is shown by the increase in visual effectiveness of their later screens.

TABLE V. Summary. Visual effectiveness relative to screen 16 of twelve fluoroscopic screens at clinical levels of excitation.

Screen	ZnS-CdS ratio	Thickness inches	Relative effectiveness	Probability value	Interpretation
16	55/45	0.0125	1.00		
10	59/41	0.0095	0.86	0.0035	different
11	55/45	0.0095	0.96	0.33	chance
17	52/48	0.0125	0.92	0.089	chance
19	55/45	0.0095	1.00		alike
20	55/45	0.0125	1.20	0.032	different
21	55/45	0.0160	1.12	0.050	different
		Type			
22	U. S. Radium "green"		0.97	0.76	chance
8	Patterson B-1		0.83	0.0016	different
13	Patterson B-1		0.96	0.44	chance
18	Patterson B-2		0.97	0.49	chance
23	Patterson B-2		1.04	0.82	chance

Letters to the Editor

Focusing Wave-Length for White Light

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May 27, 1949

IT is generally admitted that when the eye is fixed on a luminous white point, the retina is focused for the yellow radiations, the radiations of longer or shorter wave-length converging behind or in front of the retina respectively, due to the chromatic aberration of the eye. Actually we are going to see that the focusing wave-length for white light varies notably in relation to the state of accommodation of the eye.

By using Maxwellian view, I have determined the focusing wave-length of the eye, for white light and for photopic vision.[1] The upper half of the lens L is illuminated with an extended white light source W and produces a slightly extended image W' of this source (see Fig. 1). The lower half of the lens L is illuminated by means of a plane mirror m inclined at 45°, by a monochromatic point source M, and produces an image M' of this source. This image M' has a diameter of about one millimeter, and is situated at the center of W'. A wire f is stretched vertically in front of the lens L. The observer places the pupil of his eye in M', and focuses on the upper half of the wire f. The upper half of the lens L appears white, while the lower half appears of the color of the monochromatic source M. If the observer moves his head slightly from side to side, the white image W' continues to fill the entire pupil, while the monochromatic image M' describes an horizontal diameter of the pupil. Under these conditions, the lower half of the wire f seems to move relatively to the upper half, if the wave-length of the monochromatic source M differs from the focusing wave-length of the eye. In fact, if the retina is not focused on the radiations issued from the source M, the thin pencil of the monochromatic light which forms the image M' reaches the retina at a point which varies according to its distance from the axis of the eye (see Fig. 2a), *viz.*, according to the position of the head. Therefore the lower half of the wire f seems to move. If, on the contrary, the retina is focused on the radiations issued from the source M, the thin pencil of the monochromatic light which forms the image M' reaches the retina at the same point whatever the position of the head (see Fig. 2b). Therefore in this case the lower half of the wire f remains steady (in reality it is still moving, due to the spherical aberration of the eye, but very slightly). The only difficulty is to focus accurately on the upper half of the wire f (in order that the eye be in focus for the white light filling the pupil), observing at the same time the movement of the lower half. The main point is to find the wave-length of the monochromatic source M at which the movement of the lower half of the wire f ceases, when the head is moving slightly. By placing in front of the eye lenses of different powers and focusing on the upper half of the wire f, we can achieve the measurement for different states of accommodation of the eye.

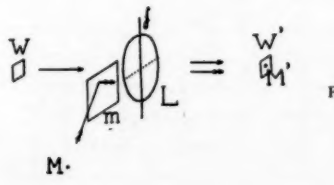

FIG. 1.

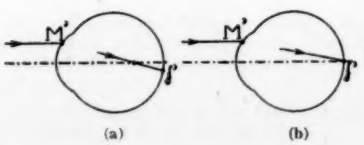

FIG. 2.

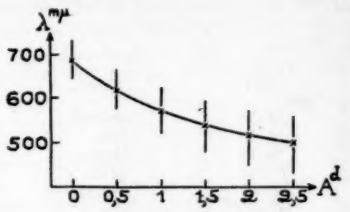

FIG. 3.

Figure 3 shows the mean of the result found on 9 eyes, with the dispersion of the measurements from one observer to another. The abscissae represent values of states of accommodation in diopters, and the ordinates represent the corresponding focusing wave-length. We see that this wave-length is in the red for the unaccommodated eye, in the yellow for an accommodation included between 0.5 and 1 diopter, and is stabilized in the green or in the blue for an accommodation higher than 2.5 diopters.

This phenomenon is extremely useful because it allows the eye, due to its chromatic aberration, to relieve notably its effort of accommodation, in white light: at close vision the eye is focused on blue radiations, the focus of which is approximately 1 diopter in front of the focus of the red radiations. All this obviously on condition that the white light used is rich enough in short wave-length radiations.

The variation of the focusing wave-length with the state of accommodation is probably correlated with the variation of the spherical aberration of the eye with the state of accommodation, of which I spoke in a preceding article.[2] The distribution of light in the retinal image is actually correlated with the spherical aberration of the eye. When accommodating, the eye changes from under-correction to over-correction, and there results variations in the retinal illumination which produce the phenomenon expounded in this article.

[1] A. Ivanoff, C. R. Ac. Sc. Paris **228**, 1156 (1949).
[2] A. Ivanoff, J. Opt. Soc. Am. **37**, 730 (1947).

Comparison of Lens Radii

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IN an investigation of the variation of grinding tools in the production of spherical surfaces, a convenient method has been developed for comparing the radii of the surfaces of a lens. In these experiments the surfaces of a thick lens of the required glass are ground, in turn, with the new and abraded tools, respectively, and the variation in curvature examined by measuring the ratio of the radii of the surfaces, R_1/R_2, by a magnification method involving the use of a microscope.

From the properties of the thick lens, it may be shown that $R_1/R_2=[M_2(M_1-1)/M_1(M_2-1)]$, where M_1 is the magnification observed when an axially placed object in contact with the first surface is viewed through the lens and M_2 is the corresponding magnification when an object in contact with the second surface is similarly examined. M_1 and M_2 are measured with a traveling microscope. The accuracy of the method is dependent on the radii and the thickness of the lens. In most instances determinations can be made to within 0.5 percent of the true value with an increased accuracy for lenses of short radii and large thicknesses.

The method has many applications in the spherometry of lens surfaces and, more recently, has been used in the choosing of components with matched surfaces and in the examination of the sphericity of quartz and glass beads produced for use in the Guild Spherometer.